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The durability of isocyanate-based adhesives under service in Australian conditions. The results from a 3 year exposure study and accelerated testing regime (Literature Review)

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www.fwpa.com.au

FWPA Level 4, 10-16 Queen Street,
Melbourne VIC 3000, Australia

T +61 (0)3 9927 3200 F +61 (0)3 9927 3288

E info@fwpa.com.au W www.fwpa.com.au



**The durability of isocyanate-based adhesives
under service in Australian conditions. The
results from a 3 year exposure study and
accelerated testing regime (Literature Review)**

Prepared for

Forest & Wood Products Australia

by

K. Van Langenberg, P. Warden, C. Adam and H.R. Milner



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Principal Researcher:

K. Van Langenberg, P. Warden
CSIRO Materials Science & Engineering
Bayview Avenue,
Private Bag 10, Clayton South, Vic, 3169

C. Adams, H. R. Milner
Timber Engineering Centre
Monash University
Clayton, Vic, 3168

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Forest & Wood Products Australia Limited
Level 4, 10-16 Queen St, Melbourne, Victoria, 3000
T +61 3 9927 3200 F +61 3 9927 3288
E info@fwpa.com.au
W www.fwpa.com.au

Executive Summary

There is a growing interest, both in Australia, and internationally, in the use of isocyanate-based adhesives for the production of structural wood components for application in a number of different service-life environments, including full exterior exposure. This interest has been driven by a number of potential advantages that these adhesives offer compared to the traditionally used phenolic and resorcinol resins. These include:

- a clear glue line
- lower resin usage
- 100% solids and hence no water to be removed from the glue line, opening up the possibility of gluing at higher wood moisture contents
- shorter cure times and hence potential increases in processing efficiencies
- no mixing of glue batches, minimising waste and reducing handling costs
- the possibility of gluing timbers that have been traditionally difficult to glue with PRF resins.

The potential benefits of these adhesives have sparked increased activity in both the fundamental research of adhesive bonding and the development of standards for application of these adhesives.

The large upsurge in interest in the adhesive scientific community has focused on the microscopic and molecular mechanisms of wood adhesion. This has extended to the topic of what makes a wood-adhesive bond durable. This research has grown over the last few years as evidenced by the number of papers presented at the Wood Adhesives 2005 symposium. One of the research topics currently being addressed is the lack of wood fibre failure when these adhesives are tested wet. The argument that isocyanate-based adhesives chemically bond with wood appears to have finally been put to rest with several groups independently determining that the isocyanate adhesive does not react with the chemical components of the wood in normal industrial operating conditions, but rather with the water that is present in the wood to form an interpenetrating network within the wood to give a good mechanical interlock.

One component, 100% solids, moisture curing isocyanate adhesives have been recently approved for use in exterior structural applications in Europe following extensive testing. There are now several examples of buildings that have been constructed using wood-based structures bonded with these adhesives. The adhesives now have more than 13 years worth of service history in Europe. The European standard EN 301/302 has been extended to include these adhesives, provided they meet the requirement of a series of additional tests focusing on their creep behaviour. These tests have been introduced after recent investigations highlighted that some of the adhesive formulations experience significant creep at higher temperatures. For approval for exterior structural use in the United States, adhesives must pass ASTM D2559 which is regarded as a severe test of durability. ASTM D3434, the Automatic Boil Test, is also regarded as a good indicator of the durability of an adhesive and has shown a very good correlation with up to 13 years worth of results from several exposure test sites. This test method is also used in the USA as a screening tool for determining the likely durable performance of new adhesives. The general trend for the development of new standards has been to create performance criteria that any new adhesive must meet. This is in contrast to the traditional standards that have been more prescriptive. This is the approach that the ISO committee is using for its adhesive standard.

There are a number of potential occupational health and safety issues in using isocyanate-based adhesives. The principal risk in using these chemicals is that they are irritants and respiratory-tract sensitisers. The Australian Government's National Occupational and Safety Commission (NOSC) has defined the permissible levels of isocyanate exposure to be $0.02\text{mg}/\text{m}^3$ on a Time Weighted Average (TWA) with a Short Term Exposure Limit (STEL) of $0.07\text{mg}/\text{m}^3$. The principal component in these adhesives is likely to be MDI, which itself has a very low vapour pressure. The risk in using these materials arises when there is a chance of making them airborne by volatilizing the adhesive or creating an aerosol of the adhesive (or particulates contaminated with the adhesive) by, for example, spraying. Such conditions are likely to exist when this product is used in the manufacture of composite wood products such as MDF, particleboard or OSB. Such a risk is significantly reduced when it is used in the manufacture of engineered wood products where it is typically applied as a liquid. Recent studies have indicated that the level of isocyanate present when used in these applications is well below the levels recommended by NOSC. These risks can be further reduced by introducing the appropriate occupational health systems and practices when these adhesives are used.

In summary, the use of the isocyanate based adhesives for the production of structural wood products is growing internationally, even in the production of exterior-grade products where there is now a 13 year service history. This is occurring in tandem with the development of performance-based standards for wood adhesives. The next stage is to determine the performance characteristics of these adhesives in Australian conditions using Australian timber species. This is the next stage of the project "*Durability of isocyanate-based adhesives in engineered wood products*" funded by the Forest and Wood Products Australia (FWPA) and the Queensland Government Department of State Development and Innovation.

Table of Contents

Executive Summary i
Introduction 3
What are Isocyanate-based Adhesives (IBAs)? 3
Occupational Health and Safety Aspects of IBAs 6
Durability of IBAs..... 10
 On the idea of covalent bonding between IBA and wood..... 10
 Durability of IBA- A review of the literature on accelerated aging..... 14
 Examples of actual in-service performance 21
Determining the durability of wood adhesives 23
 Determining the durability of non-wood structural adhesives. The influence of temperature and humidity..... 23
 Determining the durability of wood adhesives. 26
Review of international test standards 31
 Canada..... 31
 Australia 32
 ISO Approach..... 34
 European Standard 36
 ASTM standards for evaluating adhesives..... 37
Conclusions 48
APPENDIX A. Report on European and USA visit by Milner July 2005 50

Introduction

This review of the literature is part of the FWPRDC project “*PNO05.2015 Durability of isocyanate-based adhesives in engineered wood products*”. The project is collaboration between the Wood Processing unit of Ensis and Monash University’s Timber Engineering Group. The project was initiated in response to a current lack of information on the suitability of isocyanate-based adhesives (IBAs) for use in structural wood products, utilizing Australian timber species and being used in Australian conditions. There is considerable interest amongst Australian manufacturers of structural wood products for the use of IBAs as a replacement for the traditional phenolic-based adhesives. Key drivers for this include:

- IBAs are typically fast curing, allowing for the potential to improve productivity and reduce product reject rates
- The potential to utilise wood species that have been traditionally regarded as difficult to glue reliably with phenolic-based adhesives
- The use of phenolic-based adhesive systems can result in the generation of effluent streams with high potential environmental impact

This review of the current literature on the use of isocyanate-based adhesives for exterior, structural applications encompasses the following topics:

- General introduction on isocyanate-based adhesives
- Review of the occupational health and safety aspects of using isocyanate-based adhesives for the gluing of solid timber
- Summary of the current thinking regarding the durability of these adhesives, including current research in the scientific literature as well as documented case studies of their use overseas
- Brief review of how wood adhesives are tested for durability, including a brief background into the testing of other non-wood structural adhesives.
- Summary of the current standards used to determine the durability of structural wood adhesives

The scope of this review does not take into account the durability of isocyanate-based adhesives and their bonded wood products towards decay by microbial organisms or insects.

Finally, this report contains a visit report prepared by one of the authors highlighting a fact-finding mission that occurred in July 2005.

What are Isocyanate-based Adhesives (IBAs)?

The polyurethane family is an extremely large class of polymers based on the reaction of di-isocyanates with polyols and polyurethanes are used in many diverse applications, including the automotive industry (for seats, interior components, exterior panelling and engine components); the furniture industry (predominately as foamed products for cushions); the construction industry, for thermal insulation (rigid foams for use as building insulation, refrigerators and other domestic appliances) and for the production of footwear (where they are used in the production both the soles

and uppers of shoes as well as coatings for leather uppers).^{1,2,3,4,5} The use of polyurethane plastics as medical implants is also a small but emerging industry. Isocyanate chemicals having two or more isocyanate groups per molecule are used in the production of a number of different polyurethane products. The two most commercially important diisocyanates are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). It was projected that the global annual production of MDI and TDI approached 4 million tonnes in 2003, with an estimated 250,000 people involved in the global manufacture of various polyurethane products.¹

There are a large number of adhesive systems and an infinite number of possible formulations based on the chemical reactivity of the isocyanate group. To ease discussion on this class of adhesives, the name *isocyanate-based adhesive* (IBA) will be used throughout this report to indicate any adhesive that is derived from isocyanates and covers the following variations.

Polyurethanes: strictly speaking these polymers are formed between the reaction of a di-isocyanate and a polyol to form a urethane linkage. Polyols are any chemical with multiple hydroxyl groups. The most common polyols currently used are based on hydroxy-terminated polyethers, polyesters or polybutadiene.¹

The endless combination of polyols and isocyanates has made the polyurethanes easily adaptable to produce a diverse product range. Some of the applications for polyurethane adhesives include the textile industry (for use in textile lamination, rebounded foam and integral carpet manufacture), as foundry resins to bind sand to make molds for the production of steel components, and as packaging adhesives to laminate films, foils and paper.¹

API/EPI: the aqueous polymeric isocyanate (API) and emulsion polymeric isocyanate (EPI) adhesives.

Neat isocyanates: those adhesives such as MDI and polymeric MDI (pMDI) which are moisture cured adhesives with 100% active ingredients.

IBAs have been known and used for over 60 years since their discovery by Bayer in the late 1930s. Schollenberger, in his review on IBAs, listed several features that made them excellent candidates for adhesives.³ These included:

- The isocyanate chemical group is extremely reactive and can form a chemical bond with any chemical group that contains an active hydrogen atom.
- Isocyanates are very soluble in many solvents, due to their low molecular weight, and they can easily wet and penetrate into porous structures to form strong mechanical interlocks.

¹ G. Woods, "The ICI polyurethanes book", ICI Polyurethanes and John Wiley and Sons, 1987.

² B. Edwards, "Polyurethane Structural Adhesives", *Structural Adhesives. Chemistry and Technology*, **Chapter 4**, Ed. S. Hartshorn, Plenum Press, 1986, 181

³ C. Schollenberger, "Polyurethane and isocyanate-based structural adhesives", *Handbook of Adhesives*, **Chapter 20**. Ed. I Skeist, Van Nostrand Reinhold, 1990, 369

⁴ A. Pizzi, K. Frisch, L. Rumao, "Di-isocyanates as wood adhesives", *Wood adhesives; chemistry and technology*, **Chapter 6**. Ed. A. Pizzi, Marcel Dekker Inc, 1983, 289

⁵ D. Lay, P. Crankey, "Polyurethane adhesives", *Handbook of Adhesive Technology*, Ed. **Chapter 24**. A Pizzi & K. Mittal, Marcel Dekker inc, 1994, 405

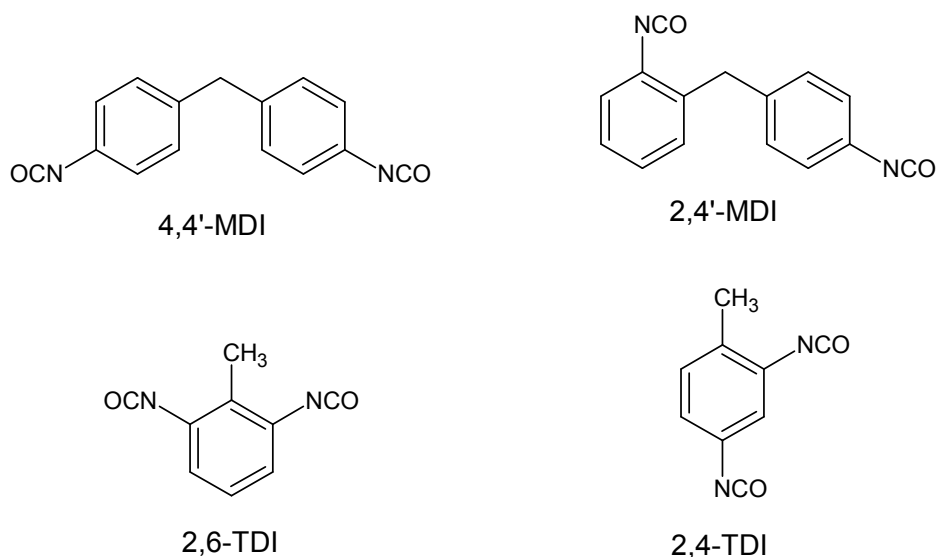
The use of polyurethanes and other IBAs is extensive and the reader is directed to a number of reviews of their chemistry and applications for more detailed information, particularly as applied in non-wood applications.²⁻⁵

As highlighted above, isocyanates are extremely reactive with any chemical functional group that has an active hydrogen. The types of chemical functional groups that can react with isocyanates are listed in Table 1, which was taken from the review by Lay and Cranley.⁵

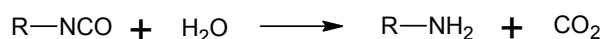
Table 1. The chemical groups with active hydrogen atoms that can react with isocyanates and their relative rate of reaction (taken from Reference 5).

Active Hydrogen Compound	Typical Structure	Relative reaction rate
Aliphatic amine	R-NH ₂	100,000
Secondary aliphatic amine	R ₂ -NH	20,000-50,000
Primary aromatic amine	Ar-NH ₂	200-300
Primary hydroxyl	R-CH ₂ OH	100
Water	H-O-H	100
Carboxylic acid	R-CO ₂ H	40
Secondary hydroxyl	R ₂ CH-OH	30
Urea proton	R-NH-CO-NH-R	15
Tertiary hydroxyl	R ³ C-OH	0.5
Urethane proton	R-NH-CO-OR	0.3
Amide	R-CO-NH ₂	0.1

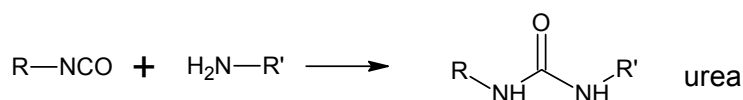
Some of the more important reactions that occur with isocyanates as an adhesive are shown in Figure 1. These include the reaction with water to form an amine (and the generation of carbon dioxide) and the subsequent reaction of the amine with another isocyanate to give a urea linkage and the reaction of an isocyanate group with a hydroxyl group (such as can be found in wood) to give a urethane linkage. It is this ability of isocyanates to react with hydroxyl groups that has led to the conclusion that isocyanates must form a covalent chemical bond with wood. However, as discussed later, it is evident that there is some doubt about this assumption.



Reaction with water to give an amine



Reaction with an amine to give a urea



Reaction with an OH group (such as in wood) to give a urethane linkage

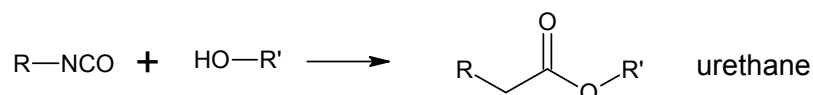


Figure 1. The major isomers of MDI and TDI and some of their chemical reactions.

Occupational Health and Safety Aspects of IBAs

The occupational health, safety and environmental (OHSE) aspects of isocyanates in the polyurethane industry have long been recognized. An excellent source of information covering all the aspects of OHSE for isocyanates can be found in “*MDI and TDI: Safety, Health and the Environment*”.⁶ Much of the information given here has been sourced from this book. Further information regarding the control of isocyanate exposure can be found in the “*Worksafe Australia Guide to Isocyanates*”.⁷ Isocyanate adhesive manufacturers are also a useful source of information.

⁶ “MDI and TDI: Safety, health and the environment. A source book and practical guide”, Ed. D. Allport, D. Gilbert, S. Outterside, Wiley and Sons, 2003

⁷ National Occupational Health and Safety Commission, “Isocyanates”, *Australian Government Publishing Service*, 1990

The physical properties of the common isocyanates used industrially are given in Table 2. Specific information regarding a given commercial wood adhesive can be found in the supplier's MSDS. Polymeric MDI (pMDI) is a liquid mixture containing monomeric MDI and higher molecular weight oligomers. Pure MDI is almost exclusively the 4, 4'-MDI monomer (98%) with traces of 2, 2'- and 2, 4'-MDI monomer. TDI can be manufactured as a single isomer or a mixture of isomers (2, 4-TDI and 2, 6-TDI). The predominant commercial form of TDI is a mixture of isomers in 80/20 ratio of 2, 4- and 2, 6-TDI.

Table 2. Physical Properties of MDI and TDI (taken from References 1 and 6).

	Polymeric MDI	Pure MDI	TDI
Appearance	Brown liquid	White solid	Colourless to pale yellow liquid
Relative density at 20°C	1.25	1.33	1.22
Melting Point (°C)	5	40	10
Reaction with water	Interacts with water slowly with the release of carbon dioxide gas		
Fire Properties	Not easily ignitable and not explosive		
Vapour Pressure (at given temperature) (Pa)	6×10^{-4} (25°C)	2.5×10^{-3} (42°C)	3.3 (25°C)

A common concept for determining hazards in the workplace is the differentiation between *hazard*, *risk* and *exposure*. In summary:

- *Hazard* is the potential for a chemical or process to do harm
- *Risk* is the probability of a chemical or process to do harm. The risk of using a product or process is the product of the exposure and the hazard.
- *Exposure* is the time or concentration that a person has to a hazard.

Exposure can be further refined into *acute* and *chronic* exposure. *Acute exposure* has been defined as a single, high concentration dose over a short time period while *chronic exposure* has been defined as the repeated or continuous exposure over an extended time period.

Exposure to isocyanates, like other chemicals, can occur by four different mechanisms:

1. Inhalation via dust, aerosols or gas vapours
2. Ingestion via the mouth
3. Absorption through the skin
4. Implantation through punctured skin such as cuts

All possible exposure routes should be avoided. Of particular concern is the inhalation of isocyanates due to the possibility of serious respiratory problems. Worksafe Australia has published the following information regarding exposure to isocyanates:⁷

Inhalation: Isocyanates have a strong irritant effect on the respiratory tract in relatively high concentrations. Some people may become sensitised to isocyanates,

even at very low levels. This sensitization may lead to the development of asthma – like symptoms such as coughing, wheezing, chest tightness and shortness of breath. These attacks can occur several hours after being exposed. Asthmatic people are more prone to sensitisation and workers with a history of asthma should not be exposed to isocyanates.

Skin: Isocyanates are skin irritants. Sensitization might occur after repeated or prolonged contact with MDI or TDI.

Eyes: Isocyanates are irritants to the eyes. Splashes of MDI or TDI can cause severe chemical conjunctivitis.

Other health effects that have been reported include liver and kidney dysfunction. MDI and TDI have very low oral toxicity.

The Australian government's National Occupational and Safety Commission (NOSC) has defined the acceptable levels of air-borne exposure for isocyanates.⁸ These are given in Table 3. The *Time Weighted Average* (TWA) is the average airborne concentration when calculated over an 8 hour work day for a 5 day working week. The *Short Term Exposure Limit* (STEL) is a 15 minute TWA which should not be exceeded at any time of the working day. This is the case even if the eight-hour TWA is within the exposure standard. Exposures at the STEL level should not be longer than 15 minutes and should not be repeated more than 4 times each working day. Furthermore, there should be a time period of at least 1 hour between successive exposures at the STEL. Further information may be found at the NOSC website.⁸

Table 3. The TWA and STEL values for exposure to isocyanates in Australia

	TWA (mg/m ³)	STEL (mg/m ³)
All isocyanates	0.02	0.07

The risk of exposure to airborne MDI can be minimised if care is taken not to vaporize it such as by heating it or making an aerosol by, for example, spraying it. The vapour pressure of MDI is very low (see Table 2). Purbond has evaluated the airborne concentration of isocyanate when their one-component moisture cure adhesive was used.⁹ The concentration of isocyanate in the air was measured in six different stages of the gluing process. These results are shown in Figure 2 and Figure 3. It is clear that, based on these results; the concentration of isocyanate is significantly lower than the allowable exposure threshold of 0.02 mg/m³ TWA (equivalent to 20µg/m³) defined by the Australian government.

⁸ See their website at <http://www.nohsc.gov.au/>

⁹ R. Studer, "Determination of isocyanate exposure resulting from the application of polyurethane adhesives made by Purbon AG, Switzerland", *Graduate thesis*, ETH Zurich, EMPA Dubendorf, 2003

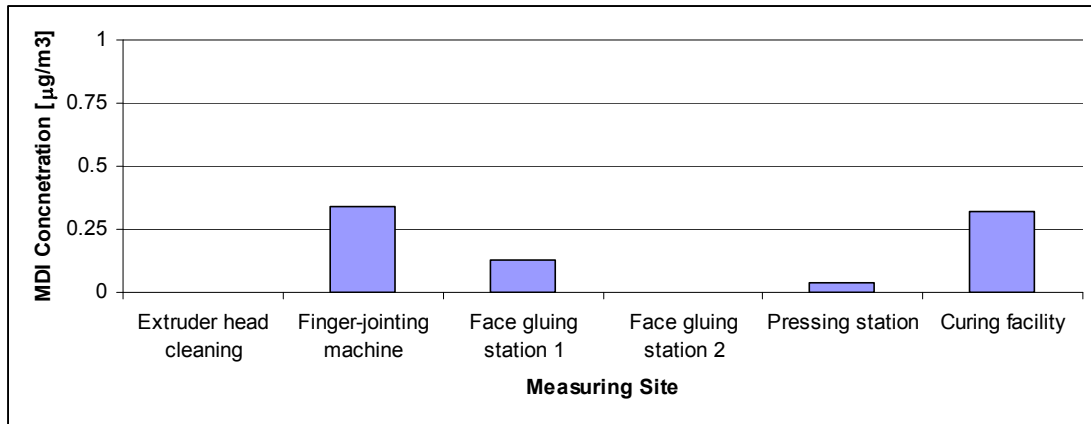


Figure 2. Concentration of airborne MDI at six stages of the gluing process (Taken from Reference 9).

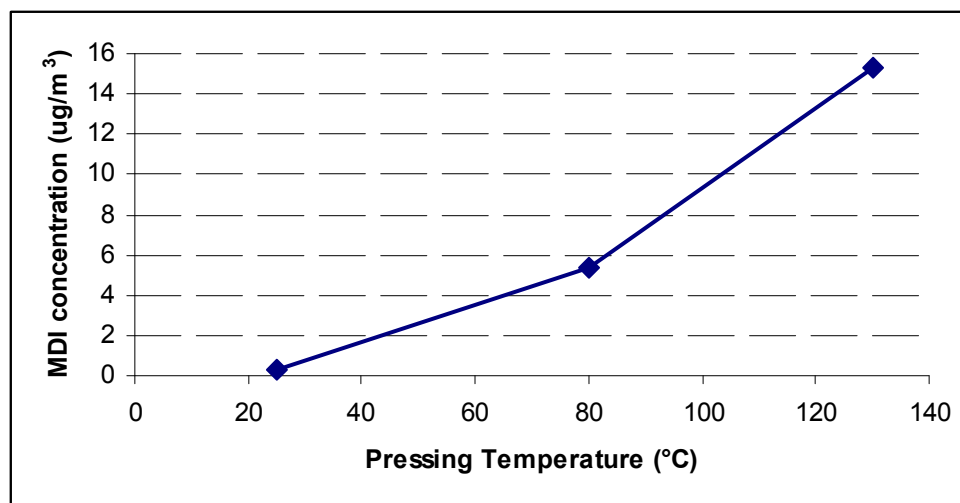


Figure 3. The influence of pressing temperature on the concentration of airborne MDI (Taken from Reference 9).

Minimising exposure to isocyanates follows the same general procedure that would be followed for the use of any chemical, including other current types of wood adhesives. The methods to minimise exposure follow a standard hierarchy based on effectiveness. These are listed below and are taken from reference 7.

- *Elimination or substitution and process modification* to eliminate the need to use isocyanates
- *Engineering controls.* It is recommended that the use of isocyanates should be done in an enclosed environment with good ventilation to ensure that atmospheric concentrations are maintained at a level lower than the exposure level. In most cases, this is not feasible and local ventilation is required. This is essential for the use of TDI or when any isocyanate is sprayed. If vaporization cannot occur then local ventilation may not be required, as long as the air concentration is kept below the exposure standard. This would appear to be the case for the use of IBAs for timber gluing where the glue is applied as a liquid.
- *Administration.* The use of policies and procedures for the safe handling and use of isocyanates. This should include a policy of routine monitoring of the workplace.

- *Personal protective equipment (PPE)* should be worn when handling isocyanates. The correct PPE will be given in manufacturers' MSDS, but should include appropriate safety glasses, gloves, shoes and overalls/lab coat.

It has been suggested that those workers who are likely to be exposed to isocyanates, particularly those that are involved in spraying isocyanates, should undergo periodic health checks. These checks should involve the monitoring of lung function. It has been stated that a significant number of people who become sensitised to isocyanates become sensitized within the first 8 weeks of daily use.

Summary

The isocyanates commonly used in industrial quantities are MDI and TDI. MDI is the predominant isocyanate used for adhesives. All isocyanates are irritants and may cause sensitization to some workers. The major risk to the health of workers appears to be exposure by inhalation. This may be caused by processes that produce aerosols, dust or vapour. MDI has a low vapour pressure at room temperature so that the two main methods of inhalation will be the creation of dust or aerosols produced, for example, by spraying. The risk of exposure to MDI, when used as a wood adhesive, is greatest in those industries that volatilize the MDI by spraying. These conditions regularly occur in the production of particleboard, MDF or OSB. When MDI is applied as a liquid by spreading or extruding, conditions typically found in the production of glulam, it has been shown that the exposure to MDI vapour is much lower than the maximum recommended safe exposure levels. Following the recommended procedures as outlined by the MDI manufacturers will significantly reduce the risk of exposure to isocyanate. Further general information can be obtained from the excellent reference book "*MDI and TDI: Safety, Health and the Environment*".

Durability of IBAs

On the idea of covalent bonding between IBA and wood

There has been much debate regarding the possibility of covalent chemical linkages between the isocyanate components of IBAs and wood. In theory it should be possible for an isocyanate to react with the hydroxyl groups in the cellulose, hemicellulose and lignin components of wood to give urethane linkages, the hydroxyl group containing an active hydrogen.

Many workers have investigated the potential for urethane linkages with wood or its components using a number of different techniques.^{10,11,12,13,14,15,16,17} Early work

¹⁰ K. Frisch, L. Rumao, A. Pizzi. "Diisocyanates as wood adhesives", *Wood Adhesives: Chemistry and Technology*, Ed. A. Pizz, Marcel Dekker, 1983, 289

¹¹ H. Deppe, "Technical progress in using isocyanate as an adhesive in particleboard manufacturing", *Proceedings, Eleventh International Particleboard/Composite Symposium*, Ed. T. Maloney, Washington State University, 1977, 13

¹² J. Frink, H. Sachs, "Isocyanate binders for wood composites boards", *Urethane chemistry and applications*, Ed K. Edwards, ACS Symposium Series 172, ACS, 1981, 285

¹³ W. Johns, "Is there an isocyanate in your future", *Proceedings, Fourteenth International Particleboard/Composite Symposium*, Ed. T. Maloney, Washington State University, 1980, 177

utilising Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC) techniques investigated the reaction of isocyanates with cellulose, lignin and wood.¹⁸ These workers found that urethane linkages can form between isocyanates and cellulose, lignin and oven-dried wood, but that no urethane linkages were found between isocyanates and wood when the wood moisture content was greater than 4.5%. Above this moisture content, the reaction between isocyanates and water (to give ureas and biurets) dominates.

Further studies by Phanopoulos *et al* used solid-state 2-D NMR techniques on isocyanate (pMDI) composites with cellulose, lignin, water and wood (aspen and southern yellow pine).¹⁹ Urethane linkages could be detected with the cellulose and lignin composites, but the reaction of isocyanates with water dominated in the wood composites. These results confirmed their earlier work which studied the effect of wood moisture content and temperature.²⁰ This work also found that the gluing of wood with isocyanates occurs through the reaction of isocyanates with water present in the wood, to give urea and biuret species that can form a cross-linked polymer matrix. Based on these results, this group proposed that a suitable model for the curing of the isocyanate-wood glue bond was one where pMDI penetrates deeply into wood cells and into the middle lamellae between the cells and reacts with the water present to form urea linkages (both linear and branched) and which form an entangled, interpenetrated network to give a strong, mechanically interlocked bond (see Figure 4). This mechanism of bonding is in good agreement with observations of resin penetration into wood using chemical state X-ray microscopy.²¹ This technique found that pMDI penetrated deeply into the wood, entering large cell lumens and wicking within the inner cell wall. The adhesive was found in adjacent cells after travelling via connecting pits. However, no evidence of penetration of the MDI into the cell walls was detected.

¹⁴ O. Wittman, "Wood bonding with isocyanate", *Holz als Roh werkstoff*, **34**, 1976, 427

¹⁵ Rowell and Ellis

¹⁶ C. Galbraith, W. Newman, "Reaction mechanisms and effects with MDI isocyanate binders for wood composites", *Proceedings, Pacific Rim Bio-based Composites Symposium*, Rotorua, New Zealand, 1992, 130

¹⁷ F. Weaver, N. Owen, "The isocyanate-wood adhesive bond", *Proceedings, Pacific Rim Bio-based Composites Symposium*, Rotorua, New Zealand, 1992, 145

¹⁸ F. Weaver, N. Owen, "Isocyanate-wood adhesive bond", *Applied Spectroscopy*, **49** (2), 1995, 171

¹⁹ S. Bao, W. Daunch, Y. Sun, P. Rinaldi, J. Marcinko, C. Phanopoulos, "Solid state two-dimensional NMR studies of polymeric diphenylmethane diisocyanate (PMDI) reaction in wood", *Forest Products Journal*, **53** (6), 2003, 63

²⁰ S. Bao, W. Daunch, Y. Sun, P. Rinaldi, J. Marcinko, C. Phanopoulos, "Solid state NMR studies of polymeric diphenylmethane diisocyanate derived species in wood", *J. Adhesion*, **71**, 1999, 377

²¹ C. Buckley, C. Phanopoulos, N. Khaleque, A. Engelen, M. Holwill, A. Michette, "Examination of penetration of polymeric methylene di-phenyl-di-isocyanate (pMDI) into wood structure using chemical state x-ray microscopy", *Holzforchung*, **56** (2), 2002, 215

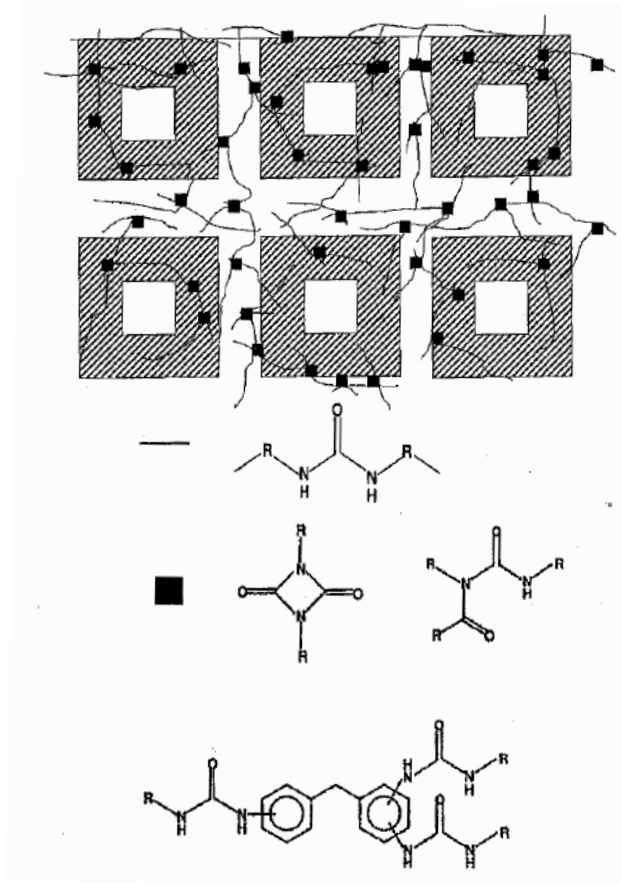


Figure 4 The model of isocyanate-wood bonding as proposed by Phanopoulos *et al* (Taken from reference 19).

Frazier *et al* have more recently examined the MDI-wood interphase in the context of OSB production.^{22,23,24,25,26} By using ^{15}N CP solid state NMR, together with ^{15}N labelled MDI, they have been able to get a clearer picture of the wood-MDI interaction than previous studies. The use of the solid state NMR technique gave the ability to probe the interface/interphase region and analyse the phase boundary interactions and interphase morphologies.²⁶

By looking at cellulose-pMDI composites at various moisture contents (0-30%) Frazier *et al* identified the cure chemistry of the adhesive.^{22,23} It was found that biuret

²² S. Wendler, C. Frazier, "The ^{15}N CP/MS NMR characterization of the isocyanate adhesive bondline for cellulosic substrates", *J. Adhesion*, **50**, 1995, 135

²³ S. Wendler, C. Frazier, "Effect of moisture content on the isocyanate/wood adhesive bondline by ^{15}N CP/MAS NMR", *Journal of Applied Polymer Science*, **61**, 1996, 775

²⁴ S. Wendler, C. Frazier, "The effects of cure temperature and time on the isocyanate-wood adhesive bondline by ^{15}N CP/MAS NMR", *Int. J. Adhesion and Adhesives*, **16**, 1996, 179

²⁵ C. Frazier, J. Ni, "On the occurrence of network interpenetration in the wood-isocyanate adhesive interphase", *Int. J. Adhesion and Adhesives*, **18**, 1998, 81

²⁶ R. Schmidt, C. Frazier, "Cross-polarization studies of interphase morphology in the wood-pMDI adhesive bondline", *Composite Interfaces*, **7** (2), 2000, 93

chemical linkages (from the reaction of urea with isocyanate) dominate at the lower moisture content conditions. Above approximately 6% moisture content, polyureas were found to dominate due to the higher levels of water present. No significant urethane linkages were detected at any of the moisture content levels studied, but it was highlighted that low levels of urethanes could be masked in the NMR spectra.

Following this work, Frazier *et al* further investigated the effect of cure temperature and time on the chemical species formed in the adhesive/wood glueline.²⁴ At low cure temperatures (less than 120°C), urea and biuret linkages were found with the biuret being dominant. At temperatures greater than 120°C it was found that the biuret structure thermally decomposed to give urea and isocyanate functional groups. As the cure time increased at these elevated temperatures, the formation of urethane linkages was suggested. These urethane linkages were postulated to be formed between the isocyanate linkages (from the decomposition of the biurets) and hydroxyl compounds in the wood. Figure 5 shows the possible reversible reactions of isocyanate in the wood according to Frazier.²⁵ Based on these results, Frazier concluded that the use of pMDI as a wood adhesive could be regarded as a 2-part adhesive system. This is due to the presence of water in the wood being essential for curing. Like the previous studies, Frazier concluded that there was no significant chemical bonding between the wood and the pMDI, due to the inability to find any evidence of significant levels of urethane linkages.

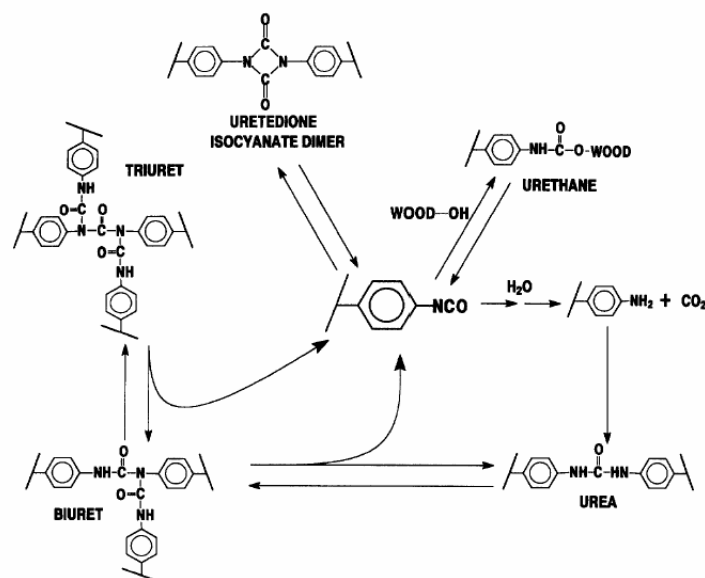


Figure 5. A summary of chemical reactions that occur in the wood/isocyanate bond line as proposed by Frazier (taken from reference 25).

Frazier *et al* extended their work by investigating the possibility of molecular interpenetration of the isocyanate adhesive into the wood in the wood-glue interphase. Frazier concluded that pMDI easily wets wood and penetrated deeply into the wood, as would be expected for a low viscosity organic liquid. The wetting of the wood surface is more energetically favourable than that of the water-borne PF and UF adhesives. As the pMDI penetrates into the wood, it causes the wood polymers to swell. From these results, Frazier concluded that the pMDI was achieving an intimate mixing with, and penetrating into, the wood at a molecular level or molecular

interpenetration. This swelling of the wood polymers has been seen in previous work by Marcinko *et al.*^{27,28,29} Others have not seen this phenomenon when different wood species were studied, indicating that molecular penetration of MDI might be species dependant.^{30,25} Based on these findings, Frazier suggested that MDI could be considered as a reactive organic solvent due its low molecular weight compared to the more traditional aqueous PF and UF systems (which are 1-2 orders of magnitude higher in molecular weight).

In summary, it appears that the concept of isocyanate-based adhesives forming covalent chemical bonds with wood is unlikely to occur in current industrial practices. There is now enough evidence from several different research groups to indicate that this does not occur due to the presence of water within the wood structure. Indeed, it has been argued that this water is critical in curing MDI in the bond line. The MDI penetrates deeply into the wood where it can react with water to form an interpenetrating network of ureas and biurets within the wood structure and that this is the mechanism of adhesive cure with wood.

Durability of IBA- A review of the literature on accelerated aging

There has been an increased interest in the scientific literature around the feasibility of determining the durability of wood adhesives. This has been particularly driven by the emergence of isocyanate-based adhesives for bonding wood, for both the production of engineered wood products or for the manufacture of composite panel products. The increased research effort in this field is supported by the fact that 15 papers describing the use or testing of IBAs were recently presented at the Wood Adhesives 2005 symposium.³¹

Scoville, in his Masters thesis, investigated the durability of pMDI adhesives using fracture testing and compared the results to a PF resin.³² Yellow polar was the wood substrate used. The technique measures the fracture energy (the energy required to separate the two wood faces of the glue line) by using a double cantilever beam (DCB) method of fracture testing. Fracture toughness has been described as the ability of a material (such as the adhesive) to resist the propagation of cracks. DCB experiments allow for the calculation of the critical crack initiation energy (G_{max}) and the crack arrest energy (G_a). Previous studies had shown that differences in adhesion glue line variables (such as resin formulation, press time and pre- and post treatments) could be detected using fracture testing that were not otherwise

²⁷ J. Marcinko, W. Newman, C. Phanopoulos, “ ”, *Proc. 2nd Bio-based Composites Symposium*, Vancouver, Canada, 1994, 286

²⁸ J. Marcinko, S. Devathala, P. Rinaldi, S. Bao, “Investigating the molecular and bulk dynamics of pMDI/wood and UF/wood composites”, *Forest Prod. J.*, **48** (6), 1998, 81

²⁹ J. Marcinko, P. Rinaldi, S. Bao, “Exploring the physiochemical nature of pMDI wood structural composite adhesion”, *Forest Prod. J.*, **49** (5), 1999, 74

³⁰ W. Gindl, T. Schoberl, G. Jeronimidis, “The interphase in phenol-formaldehyde and polymeric methylene di-phenyl-di-isocyanate glue line in wood”, *Int. J. Adhesion and Adhesives*, **24**, 2004, 279

³¹ see list of papers presented at <http://www.forestprod.org/confpast.html>

³² C. Scoville, “Characterising the durability of PF and pMDI adhesive wood composites through fracture testing”, *Masters Thesis*, Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University, 2001

discernible using more traditional internal bond (IB) tests.^{33,34} One advantage of DCB fracture testing over the traditional IB or block shear tests is that the method focuses the failure to occur within the glue line and hence information regarding the adhesive, as opposed to the wood, can be gathered. By using the DCB set-up, Scoville investigated the effect of two different aging regimes on the durability of the pMDI and PF resins. One of the regimes involved a 2 hour boil cycle followed by drying for 22 hours at 102°C. This was repeated for up to 4 cycles. The second accelerated test was a modified version of ASTM D-1037. In this test, the sample was exposed to 50°C and 100% RH for 2 hours, 102°C and 0% RH for 4 hours. This cycle was repeated.

Schoville found that the pMDI adhesive was very resistant to the boil cycle treatments, with no decrease in the fracture energies. The fracture energies were found to increase slightly (Figure 6). This increase was postulated to be due to further curing of the adhesive or the relaxation of internal stresses. In contrast to these results, the PF resin was found to exhibit a significant decrease in the fracture energies after the first cycle and then to increase slightly (not statistically significant) (Figure 6). This decrease was postulated to be due to cleavage of bonds, either in the adhesive bond line or at the adhesive-wood interface.

Similar results were found in the environmental aging tests (Figure 7). The pMDI adhesive showed a slight decrease in fracture energy after 1 cycle and it increased slightly after the second cycle. Unlike the pMDI adhesive, the PF bond line showed a significant decrease in fracture energy after each cycle.

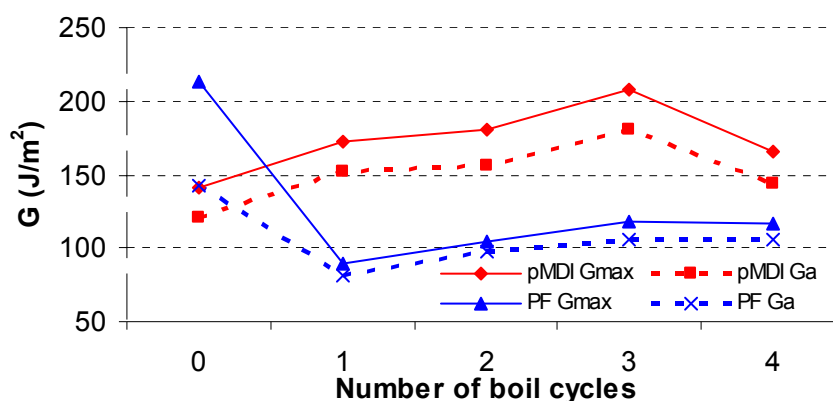


Figure 6. The effect of 2 hour boil cycles on the fracture energies of pMDI and PF adhesives from Scoville (32).

³³ J. Gagliano, "An improved method for the fracture cleavage testing of adhesively-bonded wood", *Masters Thesis*, Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University, 2001

³⁴ J. Gagliano, C. Frazier, "Improvements in the fracture cleavage testing of adhesively-bonded wood", *Wood and Fiber Science*, **33** (3), 2002, 377

Based on these results, Scoville concluded that the pMDI adhesive was more resistant to degradation than the PF adhesive when the fracture energy of the adhesive was used as a measure of durability.

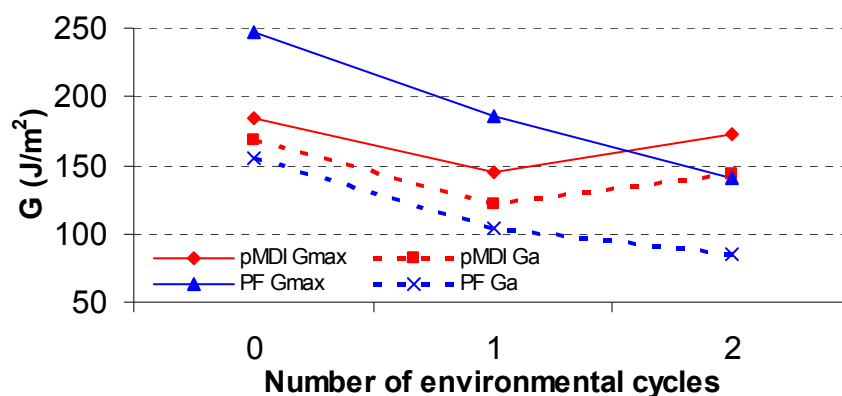


Figure 7. The effect of environmental aging cycles on the fracture energies of pMDI and PF adhesives as seen by Scoville (32).

Vrazel, as part of a larger study, looked at the effect of species, adhesive type and cure temperature on the strength and durability of structural finger joints.^{35,36} He investigated an API system and compared it to an RF system, and tested the samples for delamination after undergoing a cyclic test as outlined in the American Institute of Timber Construction (AITC) Test, T110 (Cyclic delamination procedure). This test involves a vacuum pressure soak, followed by drying at 60-71 °C before testing. He concluded that the API system was comparable to the RF resin system.

Umemura investigated the durability of aqueous emulsified polymeric MDI with water by comparing the thermal stability of water cured films with a PF control using dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR).³⁷ The isocyanate film cured with water showed a sudden decrease in storage modulus at 200°C, which recovered at 220°C. This was ascribed to the formation of a more stable structure. After 220°C, the storage modulus rapidly decreased. The PF resin showed a more stable storage modulus. It was concluded that the water-cured isocyanate films were less thermally stable than the PF resin. Further work was undertaken to study the effect of polyols on the thermal stability.³⁸ Some polyols (such as a low molecular weight dipropylene glycol polyether) showed improved thermal stability compared to the water-cured film, whilst other polyols gave an inferior performance. Plywood samples were also made and tested and the dry strengths were found to be comparable to a PF control. Other studies looked at the

³⁵ M. Vrazel, "The effect of species, adhesive type and cure temperature on the strength and durability of a structural finger joint", *Masters Thesis*, Department of Forest Products, Mississippi State University, 2002

³⁶ M. Vrazel, T. Sellers, "The effect of species, adhesive type and cure temperature on the strength and durability of a structural finger joint", *Forest Products Journal*, **54** (3), 2004, 66

³⁷ K. Umemura, A. Takahashi, S. Kawai, "Durability of isocyanate resin adhesives for wood I: Thermal properties of isocyanate resin cured with water", *J. Wood Sci.*, **44**, 1998, 204

³⁸ K. Umemura, A. Takahashi, S. Kawai, "Durability of isocyanate resin adhesives for wood II: Effect of the addition of several polyols on the thermal properties", *Journal of Applied Polymer Science*, **74**, 1999, 1807

durability of water-cured and polyol-cured adhesives after exposure to both dry heat and steam.^{39,40}

Pizzi measured the comparative creep resistance of two commercial polyurethane adhesives against two phenol-resorcinol-formaldehyde (PRF) adhesives using thermomechanical analysis (TMA) (Figure 8).⁴¹ The PRF showed a constant modulus up to 175°C, after which there was a gradual decrease ascribed to the decomposition of the wood substrate. The polyurethane adhesive showed a considerable drop in modulus at relatively low temperatures (40-80°C) and it was concluded that this indicated clear evidence of the creep behaviour of this adhesive at conditions that were likely to be experienced in actual service life conditions, particularly in summer.

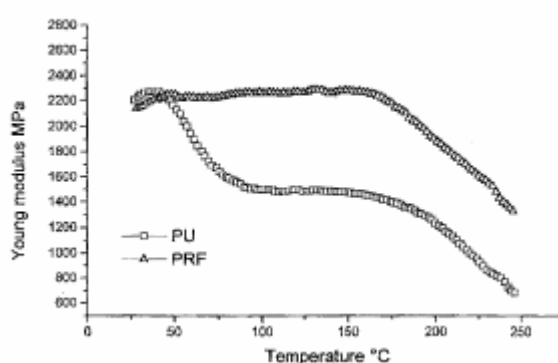


Figure 8. The creep behaviour of a PRF and PU as reported by Pizzi (Taken from Reference 41)

The issue of failure of isocyanate adhesives at higher temperatures has led to further studies. Frangi *et al* studied the shear behaviour of bond lines in glued laminated timber at high temperatures.⁴² This work was undertaken as part of a comprehensive research program at the Swiss Federal Institute of Technology (ETH) on the fire performance of timber-concrete composites.⁴² Frangi studied the temperature dependent performance of five one-component polyurethanes compared to a RF control. The performance of the adhesives was found to change from failure of the adhesive bond between the timber and the adhesive to a cohesive failure of the adhesive. This change in shear strength was found to be dependant on the polyurethane studied and occurred in the range 50-200°C. The RF resin did not show any change in shear strength below 190°C. Frangi *et al* used these results to plot the reduction in shear strength of the adhesives as a function of temperature (Figure 9). The temperature sensitivity was found to be temperature dependant and Frangi concluded that the results for one particular IBA are not valid for others. Some IBAs gave similar performance to the RF control whilst others were dramatically worse.⁴²

³⁹ K. Umemura, S. Kawai, "Durability of isocyanate resin adhesives for wood III: Degradation under constant dry heating", *J. Wood Sci.*, **48**, 2002, 380

⁴⁰ K. Umemura, A. Takahashi, S. Kawai, "Durability of isocyanate resin adhesives for wood IV: Degradation under constant steam heating", *J. Wood Sci.*, **48**, 2002, 387

⁴¹ B. George, C. Simon, M. Properzi, G. Elbez, A. Pizzi, "Comparative creep characteristics of structural glulam wood adhesives", *Holz als Roh- und Werkstoff*, **61**, 2003, 79

⁴² A. Frangi, M. Fontana, A. Mischler, "Shear behaviour of bond lines in glued laminated timber beams at elevated temperatures", *Wood Sci. Technol.*, **38**, 2004, 119

The greatest loss of shear strength occurred up to approximately 70°C with up to a 40% loss.

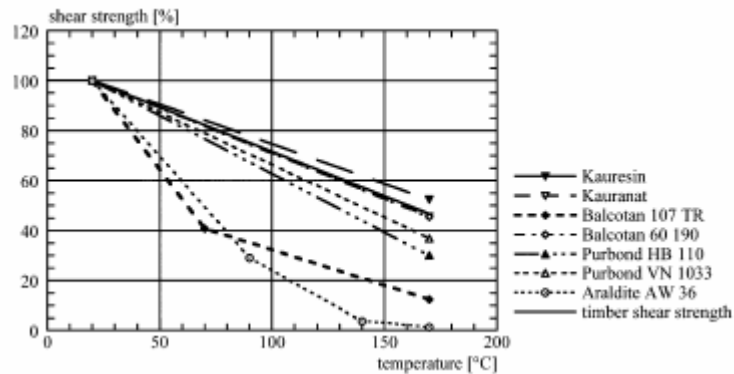


Figure 9. The reduction in shear strength versus temperature for five one-component polyurethane adhesives compared to an RF resin (Kauresin) and solid timber (Taken from Reference 42).

Richter and Steiger have further studied the thermal stability of polyurethane-bonded wood.⁴³ This work investigated the performance of 6 commercial one-component polyurethane adhesives and recorded the temperature dependant creep performance. The work also looked at the effect of glue line thickness using DTMA as well as an internally developed heat resistance test that is being reviewed for incorporation into the European standard.⁴³ It was found that the IBAs can display significant temperature dependant viscoelastic behaviour and that this behaviour was product dependant. The possibility of temperature-dependent creep in temperature ranges likely to be found in the service life of the adhesive requires the testing of any new adhesive's creep performance at elevated temperature. It was also found that this behaviour is dependent on the glue line thickness. Close contact glue line of approximately 0.1 mm gave sufficient heat resistance whilst thick glue lines (1.0mm) failed at elevated temperatures (Figure 10).

⁴³ K. Richter, R. Steiger, "Thermal stability of wood-wood and wood-FRP bonding with polyurethane and epoxy adhesives", *Advanced Engineering Materials*, 7 (5), 2005, 419

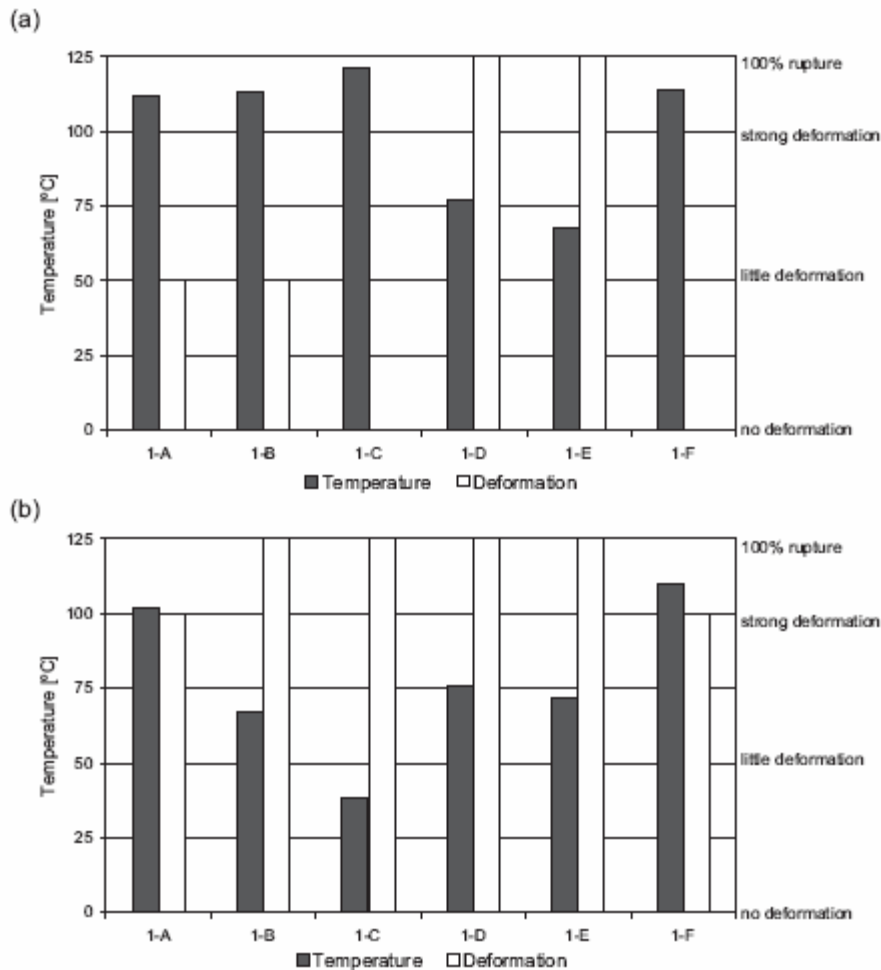


Figure 10. Failure temperature and deformation classification of 6 commercial one-component isocyanate adhesives with (a) thin and (b) thick (bottom) glue lines (Taken from Reference 43).

In response to a number of inquires, the Forest Product Laboratory in the US initiated a study on the strength and durability of 1-part isocyanate adhesives.⁴⁴ This study investigated the performance of four commercial one-part polyurethane adhesives, along with an RF control, against a number of standardised testing regimes using yellow birch and Douglas-fir substrates. These tests included block shear testing after a vacuum atmospheric pressure water soak (VAS), a vacuum pressure water soak (VPS) and a boil-dry-boil test (BDB), as well as cyclic delamination tests on laminated timber. Vick and Okkonen found that all the polyurethanes gave dry shear strengths significantly stronger than the RF control, with no significant differences in wood failure (Figure 11). In the VPS, VAS and DBD tests, the polyurethane adhesives gave similar wet shear strengths to the RF control but that the amount of wood failure was significantly less. The polyurethane adhesives were found to have wood failures of the order of 15-30% compared to 80-90% with the RF control. Vick and Okkonen concluded, based on the level of wood failure, that the RF bonds were as durable as the wood itself, but that the polyurethane bonds were considerably less durable than the RF bonds. Vick and Okkonen further investigated these polyurethane adhesives for resistance to delamination after a two cycle boil test, a

⁴⁴ C. Vick, E. Okkonen, "Strength and durability of one-part polyurethane adhesive bonds to wood", *Forest Products Journal*, **48** (11/12), 1998, 71

cyclic test as defined in ASTM 2559-92 and their resistance to deformation under a static load. The results from the cyclic boil test (identified as a moderately severe test) indicated low to high resistance to delamination, which was formulation dependant. The RF was completely resistant to delamination. All the polyurethane adhesives showed severe delamination after undergoing the cyclic delamination test. It was noted that using a hydroxymethylated resorcinol (HMR) coupling agent as a primer significantly improved the resistance of the polyurethanes to delamination.⁴⁵ The improvement was dramatic enough that the polyurethane bonded joints primed with HMR passed ASTM 2559 and were equivalent to the RF control resin used.

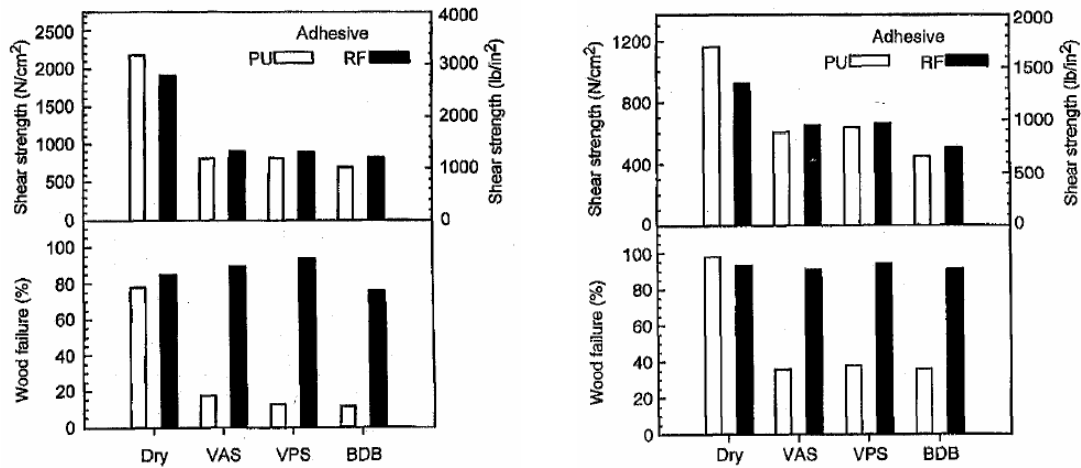


Figure 11. The shear strength and wood failure results for yellow birch (*left*) and Douglas-fir (*right*) bonded with isocyanate adhesives subjected to 4 different tests (Taken from reference 44).

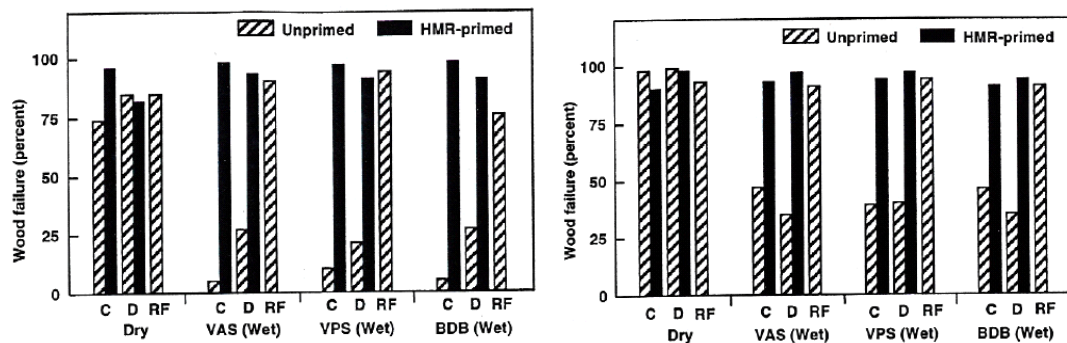


Figure 12. The shear strength and wood failure results for yellow birch (*left*) and Douglas-fir (*right*) bonded with isocyanate adhesives primed with HMR subjected to 4 different tests (Taken from reference 45).

Vick further investigated the performance of an EPI resin system under a range of different assembly conditions.⁴⁶ He found that the strength and durability of these adhesives approached the performance of the phenol-resorcinol-formaldehyde (PRF) control.

⁴⁵ C. Vick, E. Okkonen, "Durability of one-part polyurethane bonds to wood improved by HMR coupling agent", *Forest Products Journal*, **50** (10), 2000, 69

⁴⁶ C. Vick, "An emulsion polymer/isocyanate adhesive for laminating composite lumber", *Forest Products Journal*, **34** (9), 1984, 27

Rajakaruna studied the strength and durability of radiata pine bonded with 1-component isocyanate adhesives.⁴⁷ Rajakaruna's results were similar to Vick's (*vide supra*). The isocyanate adhesives were found to produce significantly stronger dry bonds than the PRF control but that the wet shear strength and wet wood failure were substantially lower.

Gindl *et al* have very recently studied the strain distribution along a bond line of either a PRF or one-component polyurethane using Electronic Speckle Pattern Interferometry (ESPI), comparing the results to those obtained using a Finite Element (FE) analysis.^{48,49} ESPI was described as an optical 3D gauging technique that allowed full field, non-contact and highly sensitive deformation measurements. By undertaking tensile lap shear tests that were monitored by ESPI, the strain distribution and strain concentrations in the area of the glue lines could be measured. Gindl *et al* are attempting to determine why isocyanate adhesives often have strength and wood failure levels comparable or higher than PRF adhesives when tested dry, but that, whilst the strength often is comparable to PRFs, the wood failure decreases dramatically when tested wet.⁵⁰ It was found that the normal and shear strains in the middle of the overlapping test area were relatively low and that they increased dramatically at the edges of the bonded area.⁴⁸ Furthermore, the increases in the shear strain were localised in the glue line itself and in an area into the wood of not more than 1mm from the glue line. Differences between the PRF control adhesive and the isocyanate were detected, with higher levels of normal and shear strain for the isocyanate compared to the PF control. The gradient of the strain was also more pronounced for the isocyanate.⁴⁸ It was also found that the penetration of the adhesives into the wood cell increased the stiffness of the wood cells.⁴⁹ Gindl proposes that the higher stiffness of PRF sets up stress concentrations in the wood-adhesive interphase, and that these stress concentrations cause the failure of the bond to occur in the wood, hence the level of high wood failure.⁴⁹ Isocyanates appear to have similar elastic properties to wood and that this limits the stress concentrations. The isocyanate adhesive has a better stress distribution. With no stress concentrations forcing wood failure, the likelihood of cohesive failure versus wood failure is increased.⁴⁹

Examples of actual in-service performance

Single component isocyanate adhesives have been developed in Europe for use in structural components such as glulam, finger joints and I-joists. They are approved for use in fully exposed, exterior structural applications if they can meet the performance requirements of the European standard (*vide infra*). These adhesives are

⁴⁷ M. Rajakaruna, "Strength and durability of radiata pine bonded with polyurethane adhesives", *Pro22: International RILEM Symposium on joints in timber structures*, Ed. S. Aicher, H. Reinhart, 453

⁴⁸ U. Muller, A. Sretenovic, A. Vinceti, W. Gindl, "Direct Measurement of strain distribution along a wood bond line. Part 1: Shear strain concentration in a lap joint specimen by means of electronic speckle pattern interferometry", *Holzforschung*, **59**, 2005, 300

⁴⁹ W. Gindl, A. Sretenovic, A. Vinceti, U. Muller, "Direct measurement of strain distribution along a wood bond line. Part 2: Effects of adhesive penetration on strain distribution", *Holzforschung*, **59**, 2005, 307

⁵⁰ W. Gindl, *private communication to Milner*, see Milner travel report (Appendix 1)

approved for exterior grade structural applications in France, Belgium, Germany and the Nordic countries.⁴³ There is now more than 13 years worth of practical experience in using these adhesives.⁵¹ These include the following buildings:

- Chesa Futura, St. Moritz, Switzerland
- Culture and congress center, Lucerne, Switzerland
- Lignopark, Germany
- New exposition Hall, Dössegger, Switzerland
- Palais de l'équilibre, Neuchâtel, Expo.02, Switzerland
- Rondorama®, Stanserhorn, Switzerland
- Sibelius hall, Lahti, Finland
- Toskana Thermae Bad Sulza, Germany
- Wine cellar in Mezzocorona, Italy
- Zang+Bahmer, Germany

Photographs of these building can be viewed at the Purbond website.⁵³

The development of these adhesives appears to have been driven largely by Collano/Purbond.⁵² There are now several examples of buildings that have used structural polyurethanes in their construction.⁵³ Much of the testing of these adhesives has been undertaken by the FMPA in Germany.⁵² The FMPA has been monitoring the creep deformation of beams manufactured using a one-component isocyanate and a PRF adhesive.^{52,54} Two beams were made for each adhesive. Each beam consists of six spruce boards, 220cm x 12cm x 15cm. The beams were set under a four point bending load with quarter point loads of 2,800kg per beam. The beams are protected against direct weathering, but open to the climatic conditions that prevail in Stuttgart, Germany. Weather data has been collected as well and have shown that the beams have been exposed to temperatures of between -11 and 32°C and relative air humidity of 15-100%. This represents seasonal wood moisture content changes of a minimum of 14% to a maximum of 19%. This experiment is still underway and has been running for 13 years. A picture showing the experiment is given in Figure 13. Creep measurements after 10 years indicate that the isocyanate adhesive exhibited similar creep deformation to the PRF control and that the rate of deflections of all the beams have decreased over this period.

⁵¹ K. Richter, M. Barbezat, A. Pizzi, A. Despres, "Thermal stability of structural 1-K-PUR adhesives", Presentation given at Wood Adhesives 2005, <http://www.forestprod.org/confpast.html>

⁵² B. Radovic, *private communication to Milner*, see Milner travel report (Appendix 1)

⁵³ See cases studies at <http://www.purbond.com/casestudies.asp?id=4&lng=en>

⁵⁴ Collano brochure



Figure 13. Photograph of the creep deformation tests that have been underway at FMPA for the last 13 years.

There have been numerous tests conducted on the ISOSET® class of water-based emulsion resins cross linked with polymeric isocyanate.^{55,68} These adhesives have been characterised as two component systems consisting of a base emulsion polymer and a cross-linking protected polymeric isocyanate. These adhesives have been approved for use under several industry specifications including structural wood and have been used for the last 26 years. The National Evaluation Service Committee has stated that their use complies with the various building codes for the manufacture of laminated structural products.⁵⁵ This class of adhesives has been used for over 20 years in the production of many different types of timber building components including LVL, I-joists, glulam beams, roof panels, wood components and composite sidings. Some of these applications have been in full exterior exposure of structural members. Ashland is currently developing a report on the historical performance of this adhesive in service.⁵⁵

Determining the durability of wood adhesives

Determining the durability of non-wood structural adhesives. The influence of temperature and humidity

An enormous amount of work has been undertaken over the last 40 years on the question of the durability of adhesives for “structural” applications in the aerospace

⁵⁵ E. Luckman, “Suitability of ISOSET adhesive for laminated wood products under exterior use”

and manufacturing industries. The vast majority of this work has focused on the durability and mechanisms of failure of adhesives for the joining of metallic or plastic substrates together. There are a number of books that have been written on this subject and the interested reader will find considerable quantities of information (beyond the scope of this review) in these books and their references.^{56,57,58}

In many of the applications studied, the ability to obtain high initial bond strengths when gluing two substrates together is relatively easy.⁵⁹ It has been found that the locus of joint failure (the path followed by a fracture surface during the breaking of a glued joint) in new, correctly prepared glue joints is often due to cohesive fracture in the adhesive layer.⁶⁰ Maintaining this strength in aggressive environments is much more difficult to achieve.⁶⁰ This is not the mechanism of failure for aged joints, where failure is often found to occur at the adhesive-adherend interface.⁶⁰ It has been stated that the most important requirement for structural adhesive joints is to continuously support the design load, under service conditions, for the expected lifetime of the structure.⁶⁰

The most aggressive environments that adhesively-bonded joints are likely to face are environments where water is present.^{59,60,61,62,63} Since water is ubiquitous in most environments (either as a liquid or vapour), it is often the greatest cause of failure for these joints, particularly for metal substrates.

The rate of adhesive bond degradation has been claimed to be dependent on a number of variables that can be classified into three broad groups.⁵⁹⁻⁶³ These are:

1. The environmental conditions (dominated by moisture and temperature)
2. The materials (adherend, adhesive and interphase)
3. Stresses the adhesive joint experiences

Environmental conditions

Moisture is considered to be the biggest enemy to glued joints.⁵⁹⁻⁶³ The mechanism by which water can dramatically decrease the strength of the adhesive joint has been described as due to a combination of a number of processes of water entering and altering a glued joint. Water can enter the joint by several pathways. These include:

1. Diffusion via the adhesive
2. Transport along the interface (also referred to as wicking)
3. Capillary ingress via cracks and crazes in the in the adhesive
4. Diffusion through the adherend (if the adherend is permeable)

⁵⁶ “*Structural adhesives. Chemistry and Technology*”, Ed S. Hartshorn, Plenum Press, 1986

⁵⁷ “*Handbook of Adhesives*”, 3rd Edition, Ed I. Skeist, Van Nostrand Reinhold, 1990

⁵⁸ “*Developments in Adhesives 2*”, Ed. A. Kinloch, Applied Science Publishers

⁵⁹ G. David, D. Shaffer, “Durability of adhesive joints”, *Handbook of Adhesive Technology*, **Chapter 7**, Ed. A. Pizzi, K. Mittal, Marcel Dekker Inc, 1994, 113

⁶⁰ S. Hartshorn, “The durability of structural adhesive joints”, *Structural Adhesives Chemistry and technology*, **Chapter 8**, Ed. S. Hartshorn, Plenum Press, 1986, 347

⁶¹ A. Kinloch, “Introduction”, *Durability of Structural Adhesives*, Ed. A. Kinloch, Applied Science Publishers Inc, 1983, 1

⁶² J. Comyn, “Kinetics and mechanism of environmental attack”, *Durability of Structural Adhesives*, **Chapter 3**, Ed. A. Kinloch, Applied Science Publishers Inc, 1983, 85

⁶³ J. Minford, “Adhesives”, *Durability of Structural Adhesives*, **Chapter 4**, Ed. A. Kinloch, Applied Science Publishers Inc, 1983, 135

Once the moisture has entered the adhesively-bonded joint, it can degrade the bond and reduce its durability by:

- Reversible altering of the adhesive (plasticization)
- Swelling of the adhesive and inducing stresses into the glue bond
- Disrupting secondary bonds across the adherend-adhesive interface
- Irreversible altering of the adhesive such as hydrolysis and cracking
- Hydrating or corroding the adherend surface

The concentration of water present is a key criterion. It has been found that the higher the level of water, the more rapid the degradation of the joint. There appears to be a minimum concentration of water required before anything starts to occur. A more detailed and rigorous examination of the various mechanisms of degradation has been discussed by Comyn.⁶²

Temperature in service can also play a role in durability. It can accelerate chemical degradation. Changes in temperature, particularly thermal spikes, can cause cracks and crazing in adhesively bonded metals due to stresses caused by thermal expansion.

Materials

Each of the materials involved in the glued joint; the adhesive, the adherend and the interphase, play a role in determining the durability of the joint.⁵⁹⁻⁶³

The adherend establishes the ultimate joint durability. The nature of the adherend, whether it be metal, plastic or wood, determines the ability for manufacturing a durable bond. The morphology of its surface can determine the degree of physical bonding (such as mechanical interlocking) that may occur. Surface pre-treatments such as grit blasting increase the surface roughness and enable more mechanical interlocking to occur. Other chemical surface pre-treatments such as the use of primers or anodising change the chemistry of the surface, making it more amenable to gluing. Interfacial imperfections between the adherend's surface and the adhesive can also accelerate debonding effects by acting as stress concentrators. The adherend's capability for expansion due to changes in temperature (measured by its coefficient of thermal expansion or CTE) plays a role in the amount of stress that the cured adhesive experiences.

The adhesive is also a critical factor in determining the durability of a glued joint. The effect of water on the adhesive is critical (*vide supra*), whether it is due to degradation due to hydrolysis or the lowering of the glass transition temperature (T_g) of the adhesive (plasticization). Other aspects of the adhesive that are important are any degradation mechanisms due to thermal or chemical effects. Since the adhesives chosen for structural applications often have been demonstrated to be chemically stable, it has been considered that chemical factors alone do not lead to serious deterioration. A further factor to consider is the modulus of elasticity (MOE) of the adhesive film. Large differences in MOE and the coefficient of thermal expansion of the adhesive and adherend can lead to the build up of stress, resulting in loss of durability. One way of reducing the MOE of adhesives for use with metallic substrates has been to introduce fillers into the glue mix.

Stress

The level of stress that a glued joint experiences appears to have a detrimental effect on the bond durability. It has been suggested that there is a certain critical stress level, below which bond failure does not occur or is not accelerated. It has also been found that cyclic stresses degrade glue bonds much more rapidly than a constant stress load.

Summary

In summary, an enormous amount of work has been undertaken trying to determine the durability of adhesives for use in bonding materials, predominately in elucidating the mechanisms of failure for adhesively bonded metals such as aluminium and titanium. It has been found that the presence of water in the service environment of the glued joint accelerates the degradation of the joint. The rate of degradation is accelerated by temperature and the presence of stress. Cyclic stresses have been found to be worse than a constant stress. A good example of the effects of humidity and stress on the durability of glued (metallic) joints can be seen in Figure 14 (taken from reference 61).

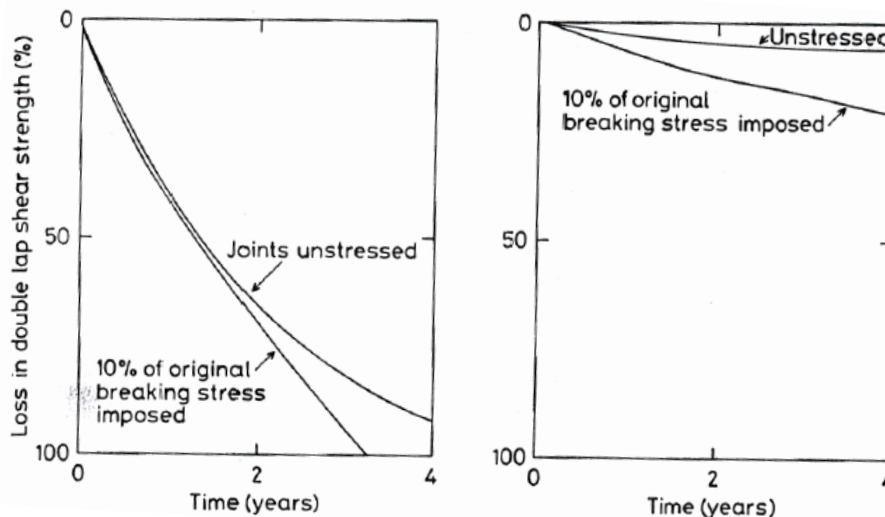


Figure 14. The effect of outdoor weathering on the strength of epoxy-polyamide bonded aluminium structural joints in a hot and wet tropical (*left*) or hot and dry desert (*right*) site. (Taken from Reference 61)

Determining the durability of wood adhesives.

The gluing of wood adds an extra complexity to the performance of the adhesive and its ability to give a durable bond. Wood is an organic composite that is adhesively bound with natural adhesive (lignin).⁶⁴ It is made up of approximately 65% polysaccharides (comprising of 42% cellulose and 23% hemicellulose), 25% polyphenolic binder (lignin) and 10% other materials (tannins, starches, minerals etc).⁶⁴ Wood has been defined as "...a porous, permeable, hygroscopic, orthotropic,

⁶⁴ T. Sellers, "Adhesives in the wood industry", *Handbook of Adhesive Technology*, Ed. **Chapter 37**, Ed. A Pizzi & K. Mittal, Marcel Dekker inc, 1994, 599

biological composite material of extreme chemical diversity".⁶⁵ It is the combination of porosity and hygroscopicity that gives wood an extra challenging dimension when it comes to gluing, that is, the change of dimensions of the wood substrate due to changes in its equilibrium moisture content. In living trees, the wood holds water as both free water in the cell lumens and as bound water within the cell wall.⁶⁵ When wood is dried, the free water is removed but a portion of the bound water remains, being attracted by hydrogen bonds to the hydroxyl groups of the cellulose, hemicellulose and lignin components of the wood. In normal service conditions, the bound water is in equilibrium with the humidity in the surrounding environment. It is this level of water that has been suggested to have the largest influence on wood as an adherend.⁶⁵ Due to its porous nature, wood can readily allow water to move through its structure. This movement of water in and out of the wood causes the wood to swell and shrink. This dimensional change of the wood can cause stresses to build up in the bond line and, if the stress is too great, the bond line can fail, leading to delamination. It is this extra factor of dimensional change due to changes in the surrounding humidity that separates the gluing of wood from other substrates such as metals and plastics. For a more detailed description of the effect of the physical properties of wood and how they affect the performance of the adhesive, the reader is directed to "Wood as an Adherend" by River, Vick and Gillespie.⁶⁵

Wood adhesives have traditionally been classified according to their stability in different service environments.⁶⁵ River *et al* have defined two different stabilities of a wood adhesive, its physical and chemical stability.⁶⁵ Chemical stability as the ability of the adhesive to resist permanent and irreversible environmental effects whilst physical stability is defined as the resistance to temporary and reversible changes to its environments such as moisture, stress and temperature. Using these definitions, Rivers *et al* use the terms durability and permanence for physical and chemical stability respectively. Wood adhesives could then be classified as:⁶⁵

- Durable: stronger, more rigid than wood, being more stable under reversible environmental effects
- Non-durable: weaker and less rigid than wood, being less stable under reversible environmental effects
- Permanent: more stable than wood under irreversible environmental effects
- Non-permanent: less stable than wood under environmental effects

These classifications are shown schematically in Figure 15 and allowed adhesives to be classified according to their performance against the environment.

⁶⁵ B. River, C. Vick, R. Gillespie, "Wood as an adherend", *Treatise on adhesion and adhesives*, Chapter 1, Volume 7, Ed. J. Minford, Marcel Dekker, 1991

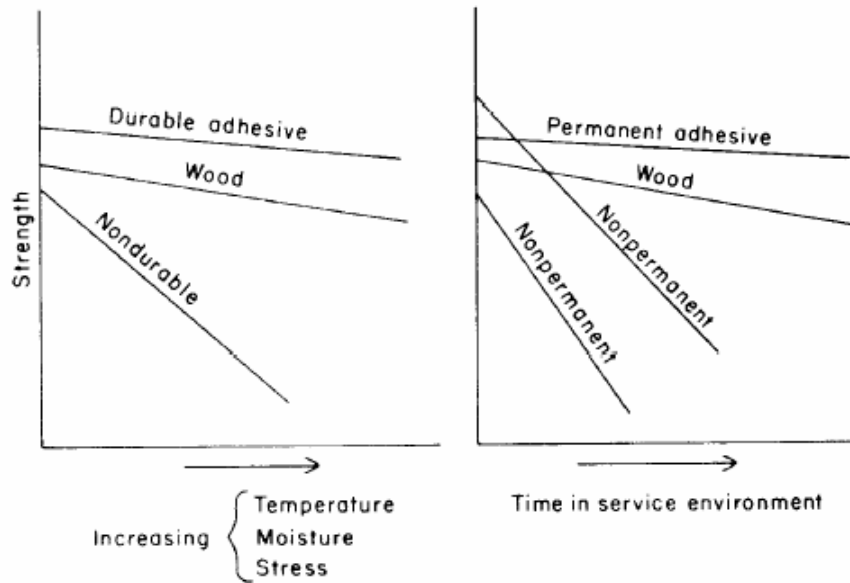


Figure 15. Schematic representation of the different definitions of adhesives as defined by Rivers *et al* (Taken from Reference 65).

Whilst this classification gives the ability to determine which adhesives are suitable for different environmental conditions, actually proving that a particular adhesive belongs to a certain classification is difficult. Much of what is currently known regarding the durability of adhesives is through the seminal work of Knight.⁶⁶ In the early 1940's, Knight prepared plywood samples glued with the then known adhesives and placed the plywood samples in four different conditions. The adhesives investigated were phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), urea-formaldehyde (UF), melamine-formaldehyde (MF), melamine-urea-formaldehyde, blood albumin, casein and starch. The environmental conditions used were full exposure in Nigeria and England, covered exposure in Nigeria and a wet room in the laboratory. This work was extended over the next decade or so. It was found that the PF or RF bonded plywood samples were the only ones to survive the exterior exposure conditions after 20 years. Many of the other adhesives had failed after 4 years exposure, except for the MF and MUF resins which failed after approximately 8 years. It is these results that have allowed the industry to recognise PF and RF resins as being suitable for full exterior usage with life spans of 50+ years, the time that has elapsed since these studies commenced.

The Holy Grail for the wood adhesives industry is to develop an accelerated test method or methods that can be used to accurately predict the potential service life of any new adhesives. Such test methods would have to be performed in a relatively short time frame, but give results that could be extrapolated (with a high degree of confidence) to predict service lives running over many decades. The absence of such tests is the largest impediment to the introduction of new adhesives types and is the reason why the current adhesives are the same ones that have been used since the end

⁶⁶ R. Knight, "The efficiency of adhesives for wood", Bulletin No. 38, Forest Products Research, HMSO, 1968

of World War 2.^{67,68} Adhesives and adhesively bonded wood products are exposed to a number of different factors that can cause degradation including moisture, heat, cyclic internal stress, air pollutants, UV light, micro-organisms and static and dynamic loads.⁶⁵ The exposure to these different conditions will vary according to the service environment of the wood material. This has meant that no single test method can accurately predict the performance of an adhesive.⁶⁵

This has not stopped many research groups from trying to develop test methods that can be used to determine the durability of adhesives, and attempting to correlate these methods to actual service life studies. An early attempt to begin such an undertaking was by the Steering Committee for Accelerated Testing of Adhesives (SCATA) in the 1960's.⁶⁷ Its goal was to “*develop accelerated test methods for predicting the service life of any glued wood product under any environmental condition and using any adhesive*”.⁶⁷ Several studies were undertaken by SCATA over a 9 year period in developing short term methods and their theoretical basis (including a continuous accelerated boil testing machine that later became the basis of ASTM 3434 and the basis for determining which of the many degradative factors should be considered in any accelerated test) but the program was abandoned after it was determined that the establishment of the long-term tests to correlate the short term tests would require over 2 million samples. Around this time, the use of chemical kinetics, chemical bond energies, hydrolysis potentials and Arrhenius reaction rates appeared to offer potential for determining the characteristics of any new adhesive. This rate process method was pioneered by Gillespie and he determined the rate of degradation of a number of adhesives subjected to water soaks, dry heat, acid and temperature.⁶⁹ The rate process method determined the thermal and chemical degradation of a wood adhesive in the absence of stress at several elevated temperatures to determine the temperature dependency of the degradation.⁶⁵ The treatment times varied from a year at low temperatures to several hours at much higher temperatures. This methodology is based on the assumption that the mechanism of degradation does not change during the process and has been successful in some applications.⁶⁵ The method does not however take the effect of stress into account, though some researchers are attempting to further develop the theoretical model to account for stress.⁶⁵

The different testing regimes developed over the years can be classified into two categories, namely single comparative and multiple-test rate methods.⁶⁵ The comparative methods involve comparing the performance of a new adhesive with one of known performance. Truax and Selbo found a good correlation between the level of delamination of small beams after a cyclic soak-dry regime and the level of delamination in exposed beams.⁶⁵ Their work formed the basis for ASTM D2559 and its shortened version, ASTM D1101.⁶⁵

The automatic boil test described in ASTM D3434 involves subjecting the adhesive bond to the major degrading factors of heat, stress and moisture in a cyclic

⁶⁷ G. Marra, “The role of adhesion and adhesives in the wood products industry”, *Adhesives for wood: Research, applications and needs*. Ed. R. Gillespie, Noyes Publications, 1984, 2

⁶⁸ H. Pagel, E. Luckman, “EPI- a new structural adhesive”, *Adhesives for wood: Research, applications and needs*. Ed. R. Gillespie, Noyes Publications, 1984, 139

⁶⁹ R. Gillespie, “Evaluating durability of adhesively-bonded wood joints”, *Adhesives for wood: Research, applications and needs*. Ed. R. Gillespie, Noyes Publications, 1984, 188

treatment.⁶⁵ Each cycle involves boiling the test specimens for 10 minutes, drying at 23°C for 4 minutes and finally drying the samples at 107°C for 57 minutes. The test may involve up to 800 of these cycles over 40 days, hence the requirement for an automated instrument.⁶⁵ Samples are removed periodically and tested to destruction to establish the rate of degradation. This test has been correlated to 12 years worth of exposure data from sites in four different locations in the United States.⁷⁰ Very good correlations were found between the results of the automatic boil test and the exposure data (Figure 16).

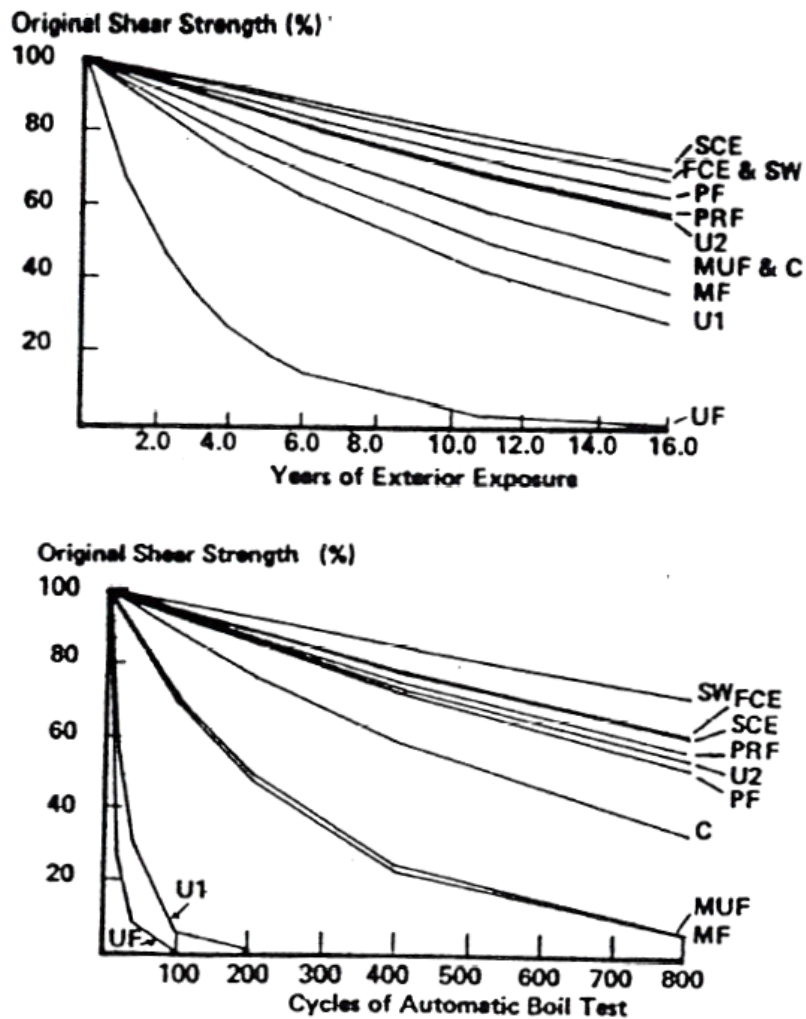


Figure 16. The correlation between the results from the 16 year exterior trial (top) and the ABT (bottom) (Taken from Reference 70). The adhesives studied were phenol-resorcinol-formaldehyde (PRF), phenol-formaldehyde (PF), melamine-formaldehyde (MF), melamine-urea-formaldehyde (MUF), casein (C), urea-formaldehyde (UF), slow cure epoxy (SCE), fast cure epoxy (FCE), urethanes (U1 and U2) and solid wood (SW).

⁷⁰ D. Caster, "Correlation between exterior exposure and automatic boil test results", *Adhesives for wood: Research, applications and needs*. Ed. R. Gillespie, Noyes Publications, 1984, 199

Review of international test standards

Canada

CSA O112.9 *Standard specification for evaluation of adhesive structural wood products (exterior use)* is a recent draft standard developed under a committee chaired by Conroy Lum. The standard does not mention the adhesive by chemical type – it simply states performance criteria that must be met and details the associated test procedures. Currently, CSA O112.9 contains provisions that address the following:

- 1) resistance to shear in the dry and wet states by compression loading,
- 2) resistance to delamination during accelerated exposure to wetting and drying,
- 3) resistance to deformation under static shear loading during exposure to high humidity, heat, or combined heat and high humidity,
- 4) resistance to fungal attack.

Resistance to shear is assessed using a traditional block shear specimen in which both strength and wood failure percentage are measured. The requirements are set out in Tables 4 and 5. The details of treatment and conditioning have been omitted for brevity.

Table 4 Median strength (MPa) requirements

Treatment and condition at test	Hardwood	Softwood
Clause 6.5.3.1 – Dry	19	10
Clause 6.5.3.2 – Wet (Vacuum-pressure test)	11	5.6
Clause 6.5.3.3 – Wet (Boil-dry-freeze test)	6.9	3.5

Not more than 50% of the specimens shall have shear strengths less than that specified in the table.

Table 5 Wood failure (%) requirements

Test Condition	Hardwood		Softwood	
	Lower Quartile ⁱ	Median ⁱⁱ	Lower Quartile ⁱ	Median ⁱⁱ
Dry	15	60	75	85
Wet	55	80	75	85

ⁱ Not more than 25% of the samples shall have a percentage wood failure less than the lower quartile value.

ⁱⁱ Not more than 25% of the samples shall have a percentage wood failure less than the lower quartile value.

The hardwood is taken to be maple (*acer saccharum* or *acer nigrum* – air dried density (ADD) 730 kg/m³) and the softwood as one of lodgepole pine (*pinus contorta* – ADD 450 kg/m³), black spruce (*picea mariana* – ADD 460 kg/m³) or douglas fir (*pseudotsuga menziesii* – ADD 530 kg/m³).

Resistance to delamination is assessed by noting the length of bond line that delaminates under 3 cycles of wetting and drying. The drying involves a temperature of 28±2°C applied for 88 hours which is a fairly benign drying regime. The tolerance on the amount of delamination is quite tight at 1%. Note that the equivalent European

and US (ASTM) standards specify higher temperature drying but compensate by allowing higher levels of delamination.

Resistance to deformation under static shear loading is effectively the ASTM D3535 creep test which is undertaken under the conditions detailed in Table 6. Details of the test specimen are given in Figure 22 below (see discussion on ASTM D3535 test).

Table 6 Environmental test conditions

Test	Condition Prior to Loading	Conditions While Under Load	Stress Level (MPa)
A	Conditioned for at least 7 days at 20±2°C and minimum 95% relative humidity	20±2°C, 95% relative humidity for a period of 7 days	2.5±0.1
B1	Conditioned to a constant mass at 20±2°C and 65±5% relative humidity (See Clause 6.5.3.1)	Minimum 70°C / ambient relative humidity for a period of 7 days	2.5±0.1 ⁱ
B2	Specimens cooled under ambient conditions following the B1 test conditioning.	Minimum 180°C air temperature / ambient relative humidity for a period of 2 hours	2.1±0.1 ⁱ
C	Cold water vacuum-pressure soak as specified in Clause 6.5.3.2	Wrap specimen to prevent moisture loss and maintain at 50±2°C for a period of 28 days ⁱⁱ	2.1±0.1 ⁱ

i The applied stress level shall be increased to compensate for the decrease in the spring constant when the creep jig is heated to 50°C, 70°C and 180°C. This can be determined by comparing the spring constant of the spring at room temperature to that when the spring is heated to the specified temperature.

ii The wrapping shall be clear flexible film (such as polyvinylidene chloride) with sufficient thickness to resist puncture. The seams shall be sealed using sheathing tape or a similar product with sufficient flexibility and resistance to heat. During the load period, there should be condensation visible on the inside surfaces of the wrap to assure that the specimen moisture content is above the fibre saturation point.

Limits placed on the permissible creep are given in Table 7. It should be noted that the values at which these limits should be set is currently being debated within ISO TC 165.

Table 7 Creep limits imposed by CSA O112.9

Environment	Creep on a single bond line (mm)	Average across all bond lines (mm)
A, B1, C	0.05	0.25
B2	0.60	2.90

Resistance to fungal attack is undertaken using an ASTM D4800 test and is required only for those adhesives containing amylaceous and/or protein based components. It is of no interest in the context of polyurethane adhesives.

Australia

Currently AS/NZS4364 *Adhesives, phenolic and amino-plastic, for load-bearing timber structures-Classification and performance requirements* is a clone of EN301 (requirements) and EN302 (test procedures), where the EN designation indicates the European origin of these standards. AS/NZS4364 combines the two into a single

document with the test procedures included as a series of appendices. Unlike CSA O112.9, AS/NZS 4364 is applicable to phenolic and amino-plastic adhesives only. There is no provision to use other classes of adhesive. This has been an impediment to the introduction of adhesives of different chemical types. Under AS/NZS 4364 Type I and Type II adhesives are defined. The climatic conditions under which they are to be used are detailed in Table 8.

Table 8 Adhesive types for use in different climatic conditions according to AS/NZS4364

Temperature	Climatic equivalent to	Examples	Adhesive type
>50°C	Not specified	Prolonged exposure to high temperature	I
≤50°C	>85% r.h. at 20°C	Full exposure to the weather	I
	≤85% r.h. at 20°C	Heated and ventilated building Exterior protected from the weather Short periods of exposure to the weather	II

Usually Type I is a phenolic type and Type II an amino-plastic such as urea-formaldehyde or melamine-urea-formaldehyde.

To further clarify which adhesives can be used in which environments, the technical committee in charge of this Australian standard, TM004, has, in the development of AS/NZS 1328 *Glued laminated structural timber Part 1: Performance requirements and minimum production requirements*, interpreted the information in Table 8 in terms of service classes; see Table 9.

Table 9 Type of adhesive for given service conditions (Taken from AS/NZS 1328 Table A1)

Service class	Description	Timber e.m.c	Temperature	Adhesive	
				Type	Example
1	Interior	≤12%	<50°C	II	Melamine-urea
2	Exterior but protected	≤18% untreated timber	<50°C	II	Resorcinol Phenol-resorcinol Polyphenolic (tannins)
		≤20% multi-salts treated softwoods			
3	Exterior	Any	Any	I	Resorcinol
			Any	I	Phenol-resorcinol Polyphenolic (tannins)

The tests contained in AS/NZS 4364 are outlined briefly below.

1. The bond strength of tension shear specimens tested without any climatic treatment is required to meet minimum strength requirements when tested on beech. Two bond line thicknesses of 0.1 and 0.5 mm, are tested. It is made clear that this differs from amino-plastic and phenolic adhesives which are tested at 0.1 and 1 mm. In Europe, isocyanate-based adhesive bond lines in excess 0.5 mm are regarded as something to be avoided. This fits in with the notion of isocyanate-based adhesives being thought of as poor gap filling adhesives.
2. The resistance to delamination after climatic treatment (vacuum-pressure soaks) is evaluated. To pass, the delamination percentage adhesive must not

exceed 5% on any bond line. Details of the climatic treatment are given in Table 11 which compares the requirements of various standards.

3. The tensile strength perpendicular to the bond line and perpendicular to the grain is required to meet a strength requirement of 5 *MPa* after cyclic moisture treatments given in Table 4.
4. The effect of wood shrinkage on the shear strength is again after cyclic moistening and drying. The requirement is that the specimen shear strengths not be reduced below 1.5 *MPa*.
5. Static loading is used to load specimens in compression shear. The bond lines are subject to a shear stress of 3 *MPa* and placed in climate chambers. Three different climates are used, each lasting 14 days or, counting all climates, for a total of 42 days. They are observed periodically to determine the time to failure. At the end of the 42 days, they are removed and, if at least 5 specimens are intact, the bond line slippage is measured to the nearest 0.01 *mm*.

Recent approaches by adhesive companies for a change to Australian Standards that would permit the use of isocyanate-based adhesives have led to TM004 looking at a new adhesive standard modelled along the lines of CSA O112.9. Some early drafts were prepared but this work got overtaken by events. The Timber Standards Coordination Group (TSCG), a committee of the Chairmen of the various timber standards committees of Standards Australia, has taken the approach that, in view of internationalisation and the World Trade Organisation treaty with its emphasis on ISO standards, it would be a better approach to focus our efforts on developing an ISO standard.

ISO Approach

The International Organisation for Standardisation (ISO) is a network of national standards institutes of 156 countries.⁷¹ It is a non-government organisation that is attempting to establish international standardisation of testing and products.⁷¹ The technical committee charged with developing an international standard for adhesives, TC 165, is chaired by one of the authors, H R Milner. It is proposing that the ISO standard will consist of the Canadian standard (CSA O112.9) with some additional tests to assess:

- hydrolytic stability – ASTM D4502,
- gap filling capacity, but one not required for adhesives used in glulam, LVL, plywood, I-beams,
- strength at pre-ignition temperatures (230°C), possibly combined with assessments of glass transition temperatures.

⁷¹ see the ISO website at <http://www.iso.org/>

The hydrolytic stability test is based on chemical kinetics, which provides a method for predicting the rate at which chemical reactions take place. It is used in conjunction with the Arrhenius law which predicts, quantitatively, how reaction rate is temperature dependent. It is theoretically possible, if the adhesive is deteriorating chemically, to convert the degradation rate at high temperature to the rate at typical service conditions. The Canadian/ISO approach differs from the European in that the latter does not refer to the adhesive chemical type. For this reason, it is unreasonable to assume that a new adhesive is automatically hydrolytically stable.

The method sounds difficult to implement but is simple in practice. The kinetic laws are written, scientifically, in terms of the rate at which moles of substance are consumed. In ASTM D4502 it is adhesive bonds that are consumed and it is assumed that this will be reflected in a loss of shear strength detected by measurements taken on block shear specimens. A modification which is before ISO TC 165 is that the wood grain needs to be inclined at an angle to the bond surface; see Figure 17. This angle and the direction of the shear force sharply curtails the value of wood failure. The rationale for this is believed to be that the measurement of wood shear strength will reveal very little about what is going on chemically with the adhesive. The angle of the wood grain should not exceed 10°, as this would alter to too greater a degree the bonding conditions.

Gap⁷² filling capacity is critical for any adhesive required for fulfilling a field gluing role, but not for adhesives where the gluing is with products where gaps do not, or at least should not, exist, such as with finger joints, face and edge joints in glulam, LVL, plywood, OSB, particleboard etc. It is critical though for adhesives used for grouted steel and fibreglass bars embedded in timber beams where the gaps can be up to 3 mm or more. It was recognition of this fact that led to the conclusion that some form of performance labelling of adhesives was required, whereby adhesives could be chosen according to the role that they were required to perform.

Pre-ignition strength, taken to mean strength at 230°C according to a recent draft ASTM standard, has been brought up as an issue on TC 165. In part it is covered by creep testing at 180°C, required by CSA O112.9. This matter is still under debate at the time of preparing this report.

⁷² An adhesive that is not gap filling should still be required to function at an acceptable level with gaps of up to 500µ.



Figure 17 Modified block shear specimen that curtails wood failure.

European Standard

All structural wood adhesives

Under European standards, all phenolic, amino-plastic and one-component polyurethane adhesives are required to meet criteria detailed in EN 301 following tests detailed in EN 302. These test methods are identical to AS/NZS 4364.

One component polyurethane adhesives only

In addition to the EN301/302 requirements, one component PURs are required to meet further requirements detailed in prEN WG4 01.7 *Adhesives, one component polyurethane, for load bearing structures – Classification and performance requirements*. The test procedures are detailed in prEN WG4 02-2 *One component polyurethane adhesives for load bearing timber structures – Test methods – Part 2: Static load test of multiple bond line specimens in compression shear*. In summary, one-component polyurethanes are required to meet the existing EN301 requirements for adhesives and additional requirements which are effectively creep deformation and creep rupture tests. The motivation for these additional tests arises out of the observation that polyurethanes tend to exhibit excessive high temperature creep, behaviour that is more apparent with thick bond lines ($> 500\mu$).

The CEN adhesive standards function in the following fashion. Two adhesive types are recognized, Type I and Type II. Type I can be used in Service Classes 1 (heated and ventilated building), 2 (covered outdoor exposure), 3 (full weather exposure). Type II can only be used in Service Classes 1 and 2.

Under prEN WG4 01.7⁷³ the following tests are carried out:

Table 10

bond strength in longitudinal tensile shear	Required for phenolics, amino-plastics and single component PURs. For PURs the performance requirements are set out in prEN WG4 01.7 and the test methods in EN 302.
resistance to delamination	
tensile strength perpendicular to the bond line after climatic treatment	
effect of wood shrinkage on the shear strength	
static load test of specimens loaded in compression shear (two forms of test described – it is optional which one is used)	PURs only and designed to test their creep resistance. The performance requirements are set out in prEN WG4 01.7 and the test methods in prEN WG4 02-2.
creep deformation test at cyclic climate conditions with specimens loaded in shear	

ASTM standards for evaluating adhesives

The American Society for Testing and Materials (ASTM) was formed over a century ago.⁷⁴ It is one of the largest voluntary standards development organisations in the world and has developed a number of standardised test methods for the evaluation of adhesives and adhesively-bonded materials. A full list of its adhesives' test methods can be found in Volume 15.06 "Adhesives" and encompasses the testing of adhesives for use with metals, plastics and wood.⁷⁴

ASTM D 905 – 03 Standard test method for strength properties of adhesive bonds in shear compression loading

This test method covers the determination of the comparative shear strengths of adhesive bonds for bonding wood and other similar materials, when tested on a standard specimen under specified conditions of preparation, conditioning and loading in compression. This test method is intended primarily as an evaluation of adhesives for wood.

The test is effectively the classical block shear test that has been an integral part of timber testing standards, including Australian Standards. It has ASTM origins dating from 1947.

⁷³ Under the the CEN system for denoting standards the pr prefix denotes that the standard is in its very early stages of development. The WG4 designation indicates that the standard is being developed by Working Group 4.

⁷⁴ See the ASTM website at <http://www.astm.org/>

It is a curious test in that not only is the strength of the test assembly measured and recorded but also the percentage wood failure. The strength measures are some undefined combination of the substrate (wood) strength and the adhesive itself or, possibly, the inter-phase region. It is actually difficult to say precisely what is being measured although the test does, with reasonable accuracy, evaluate the strength of the bond line if that is taken to mean the mix of adhesive, inter-phase zone and substrate.

The data obtained in this test are never used in practice in engineering design and is therefore a relative strength test only.

ASTM D 906 – 98 Standard test method for strength properties of adhesives in plywood type construction in shear tension loading

“This test method covers the determination of the comparative shear strengths of adhesives in plywood-type construction when tested on a standard specimen and under specified conditions of preparation, conditioning and testing.” This is an exact quote from D906.

Three-ply panels are manufactured from rotary peeled veneer with the core thickness approximately twice that of the face veneers. Cuts are made through the assembly to produce the test specimens shown in Figure 18. The test load is applied by having the peeler checks open up rather than closed.

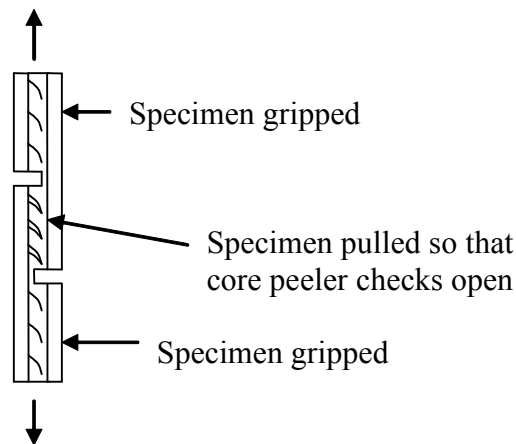


Figure 18 Method of cutting and loading ASTM D 906 specimens.

It is difficult to say what property of the adhesive this test is actually attempting to measure about the adhesive. Referring to the specimen shown in Figure 18, load is transmitted through the outer plies to the central bond lines thence to the core and then out through the lower plies. The variation of stress is of the form shown in Figure 20. Large peaks of shear stress exist at the cuts and are relatively small in the central part of the bond line. What is most likely is that the assembly will fail with rolling shear occurring in the transverse plies. It is hard to determine what the test says about the adhesive itself.

ASTM D 1151 – 00 Standard practice for effect of moisture and temperature on adhesive bonds

“This practice may be used to determine the performance, for suitable materials, in terms of any desired strength property of adhesive bonds. Test conditions of temperature and moisture only are here specified. The duration of exposure is dependent upon the nature of the adhesive and the type of specimens and will, therefore be covered by material specifications.” This is an exact quote.

This is a generic test to determine the effect of different temperature and humidity on the adhesive. It appears to be in the same class of tests as ASTM D4502

ASTM D 1183 – 03 Standard practice for resistance of adhesives to cyclic laboratory aging

“This practice provides information on the resistance to cyclic laboratory aging.” This is an exact quote.

This standard is a generic test method for testing adhesives after being exposed to a series of cyclic laboratory aging tests.

ASTM D 2339 – 98 Standard test method for strength properties of adhesives in two-ply wood construction in shear by tension loading

“This test method covers the determination of the comparative shear strengths of adhesives when tested on a standard specimen and under specified conditions of preparation, conditioning and testing. The test method is applied only to adhesives used in bonding wood to wood.” Again this is a precise statement of the scope of the test taken directly from ASTM D2339.

The substrate is rotary peeled or sliced veneer 1.6 mm thick, but other thicknesses can be used.

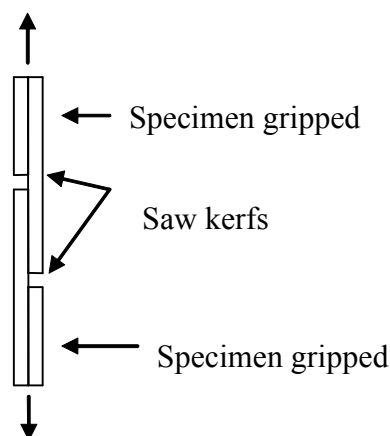


Figure 19 Method of cutting and loading ASTM D 2339 specimens.

As with the ASTM D906 test method, the standard incorrectly refers to measuring the shear strength of the adhesive rather than the shear strength of the bond as a whole. It differs from the D906 test in that the grain direction of the wood is parallel to the

applied loading. The standard also requires the recording of the percent wood failure which highlights an anomaly – if high levels of wood failure exist then wood shear rather than adhesive shear strengths are being measured.

It is a feature of the specimens shown in Figure 19 that a stress concentration exists at the point in the vicinity of the saw kerf (Figure 20). Thus while the specimen works well for comparative measures of shear strength, the data cannot be used in engineering design as the real stress distribution is unknown.

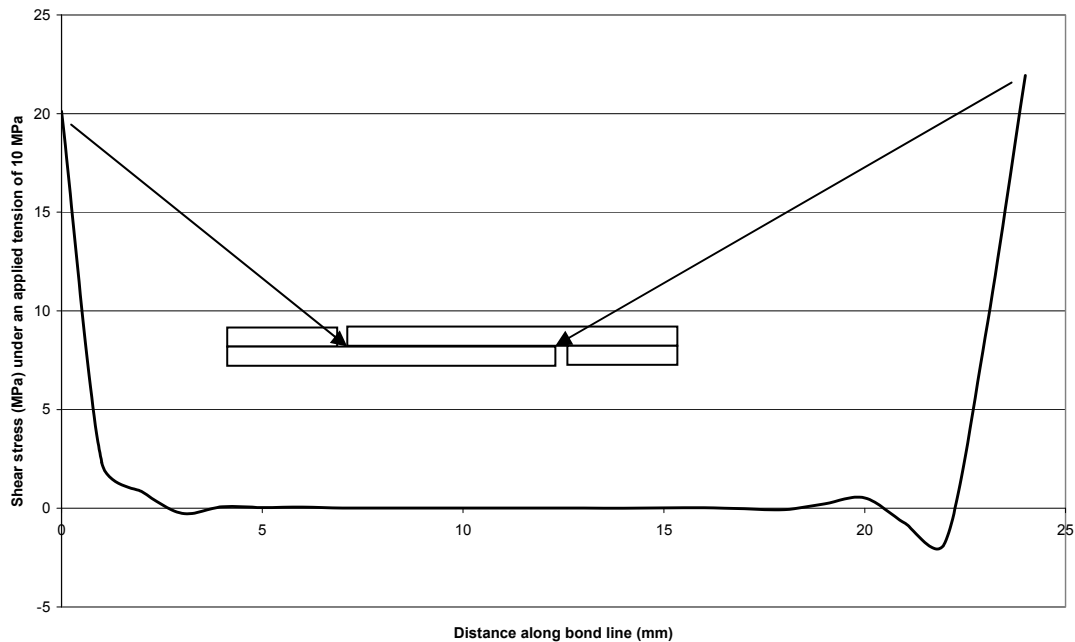


Figure 20 Variation of shear stress along the bond line in ASTM D2339 test

ASTM D 2559 – 04 Standard specification for adhesives for structural laminated wood products for use under exterior (wet use) exposure conditions

This specification covers adhesives suitable for the bonding of wood, including treated wood, into structural laminated wood products for general construction, for marine use, or for other uses where a high-strength waterproof adhesive bond is required. This standard is regarded as an extreme durability test and is used as the predominant test method for determining durability of new adhesives in the USA. There is some conjecture as to whether this standard is sufficient to use as an indicator of long term durability, with others proposing that ASTM D3434 is a better alternative.⁷⁵

ASTM D2559 is a potential candidate model for the development of an international standard for adhesives accepted as functional under ISO Service Class 3 (full outdoor exposure) conditions. The specification requires that the adhesive demonstrate the following qualities.

⁷⁵ M. Goerger, “Melamine formaldehyde adhesives for use in engineered wood products”, Presentation given at Wood Adhesives 2005, <http://www.forestprod.org/adhesives05goerger.pdf>

- When tested in accordance with ASTM D905 the block shear specimens are required to demonstrate a shear strength that is 90% of the strength of solid wood tested in accordance with an ASTM D 143 test.
- When tested in accordance with a cyclic delamination methodology described within ASTM D2559 itself, that delamination shall lie below prescribed levels given in Clause 15.4.1. Specifically this means delamination shall not exceed 1% on any one bond line for softwoods and 1.6% for hardwoods. The exposure regime consists of wetting, drying at 65.5°C for 22 h, steaming at 100°C for 1½ h, pressure soak for 40 min then a repeat of the first cycle.
- When tested in accordance with ASTM D3535 (see below) a deformation no greater than 3.63 mm for the overall assembly of bond lines shall be observed. The test is undertaken at 71°C and ambient humidity and also at 27°C and 90% relative humidity. The test is essentially one of creep deformation under a shear stress of 1.65 MPa.

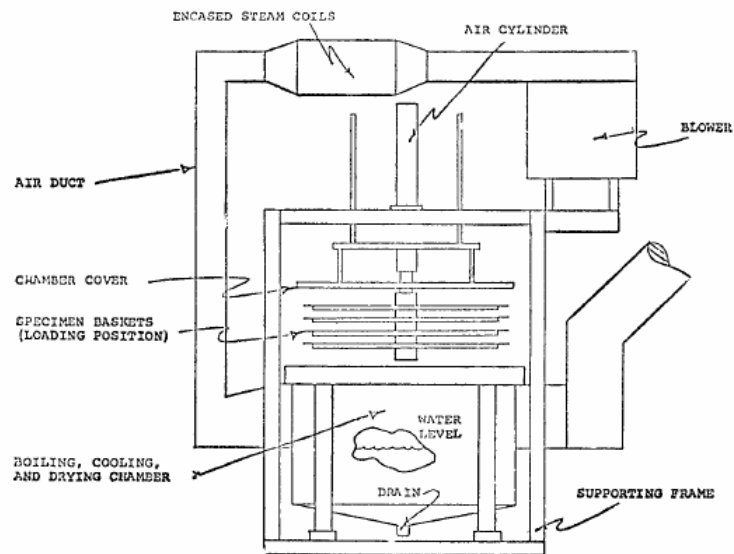
The ASTM D 2559 test methods are truly tests that assess the adhesive and are, according to European prescriptions, ones that should be applied to PURs.

ASTM D 3434 – 00 Multiple-cycle accelerated aging test (automatic boil test) for exterior wet use wood adhesives

“This test method is a procedure for testing the durability of wood adhesives that may be suitable for exterior (wet use) exposure conditions. The possible use of adhesives suitable for evaluation includes, but is not limited to, those used for laminating large members, manufacturing plywood, or fabricating wood joints such as finger or scarf joints. This practice is not suitable for interior type glues.”

This is one of the test methods that was developed under the SCATA program in the 1960's (*vide supra*). It is an extreme test that measures the ability of a wood adhesive to survive the stresses of water, stress and heat. The test involves subjecting the adhesive to a large number of boil-dry cycles (up to 800 cycles). There is a good correlation between the results of this test and at least 12 years worth of actual exposure data (*vide supra*). It requires the performance of a new adhesive to be tested against an adhesive of known durability, such as a resorcinol-formaldehyde adhesive. There is only one of these Automatic Boil Testing instruments in the world and it is owned by the Weyerhaeuser organisation who offer the test on a fee for service basis. This test is a requirement for the evaluation of new adhesives in the USA, along with ASTM D 2559.

(a)



(b)



Figure 21. Schematic (a) and photograph (b) of the Automatic Boil test instrument as described in ASTM 4343.

ASTM D 3433 – 00 Standard test method for fracture strength in cleavage of adhesives in bonded metal joints

“1.1 This test method covers the determination of fracture strength in cleavage of adhesives when tested on standard specimens and under specified conditions of preparation and testing.

1.2 This test method is useful in that it can be used to develop design parameters for bonded assemblies.”

At first sight this method appears to be of no value in assessing wood adhesives but it has been used in a modified form to study the cleavage strength of bond lines which is the primary mode of failure when bond lines delaminate. The test is based on fracture mechanic principles that have a distinguished history in predicting the failure of

materials. This test is similar to ASTM D3762 and D 5041. This methodology has been adopted by Frazier *et al* in their determination of durability of wood adhesives (*vide supra*).³² When combined with an accelerated weathering test, where the doubly tapered cantilever replaces the block shear it allows predictions of how hydrolytic stability of an adhesive is degrading with time⁷⁶. The test specimen is constructed in such a way that the wood grain direction is inclined to the bond line such as to inhibit wood failure and confine the fracture surface to the bond line itself. This test methodology could be further improved by developing a technique based on the following principles;

- use ASTM D4502 to establish that an adhesive is hydrolytically stable (replace block shear with fracture specimens according to D 3433) – this tests for what is known as cohesive strength,
- if chemical degradation cannot be detected, prepare a second set of specimens that are moisture cycled, while under load, according to the number times that sustained high humidity conditions occur in a 30 year lifetime of a bonded wood product – this tests for what is know as adhesive strength.

Large moisture changes occur in the interior of wood only if moist conditions are sustained over a period 4 to 5 days; diurnal variations have no effect.

ASTM D 3535 – 00 Standard test method for resistance to deformation under static loading for structural wood laminating adhesives used under exterior (wet use) exposure conditions

This test method covers adhesives suitable for the bonding of wood, including treated wood, into structural laminated wood products for general construction, for marine use, or for other uses where a high-strength deformation-resistant, waterproof adhesive bond is required.

The test method is one of creep deformation assessment. An assembly of test blocks, (Figure 22), is subjected to shear and the shear deformation is measured. A shear stress level of 1.65 MPa is used which is at relatively high level for softwoods under permanent load. The limit set in ASTM D 2559 of 3.63 mm over 15 bond lines means that 0.24 mm is the average set, i.e., 240 μ . Given that a PUR bond line is somewhere in the range of 100 – 200 μ , this is sufficient shear deformation that it can be presumed that bond lines would tend to rupture at this level. Until experience is gained with this test, it is difficult to decide if it constitutes a shear deformation or shear rupture test.

⁷⁶ The ASTM D4502 test makes no attempt to stress the bond line. It simply attempts to chemically (hydrolytically) degrade the bond line by subjecting block shear specimens to moist-hot conditions whence chemical degradation is accelerated.

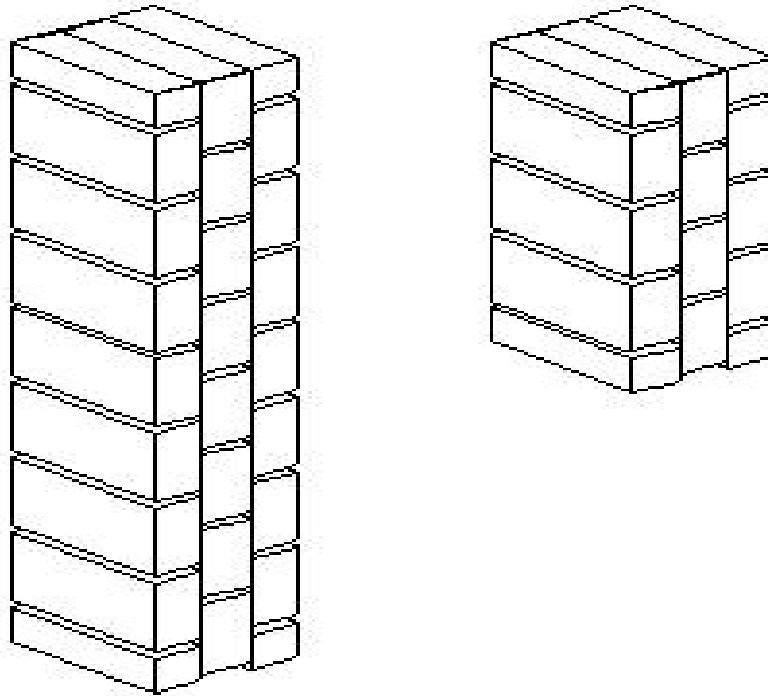


Figure 22 ASTM D3535 and CEN shear deformation test specimens. The CEN specimen is half the length of the ASTM D3535 specimen.

ASTM D 4502 – 92 Standard test method for heat and moisture resistance of wood-adhesive joints

The purpose of this test is to estimate the resistance of adhesive-bonded joints to thermal and hydrolytic degradation. The method purely seeks to assess the adhesive for signs of chemical degradation. It does not account for the effects of stress or for cyclic or variable temperature or moisture levels.

It consists of aging unloaded block shear specimens under varying temperatures and moisture levels and observing the loss of shear strength. The technique effectively assumes that the destruction of adhesive bonds will be reflected in the loss of strength and that this loss of adhesive bonds will follow a first order chemical kinetic law where the rate of loss depends on the concentration of adhesive bonds and moisture level, taken as constant. The Arrhenius Law is used to assess the constants necessary to apply the law and thus reduce the degradation rate back to the levels to be expected at typical service conditions. In reality, the test is more of a comparative test since control specimens involving the use of a proven PRF adhesive are run simultaneously and the degradation rates of the two adhesives compared.

ASTM D 4680 – 98 Standard test method for creep and time to failure of adhesives in static shear by compression loading (wood-to-wood)

This test method covers determination of time-dependent properties of structural wood adhesives in wood-to-wood bonds when specimens are subject to shearing stresses at various levels of static load, constant temperature, and relative humidity.

A block specimen is used and placed in a spring loaded device that maintains a constant load. Both creep deformations and time to failure can be observed with this test but the equipment required is quite elaborate. Thus the test is both a creep deformation and creep rupture test.

There is an interesting philosophical debate as to whether or not a creep deformation test is at useful. Those who maintain that it is have considerable difficulty in arguing why it is an important factor in the case of the bonding of many adhesively bonded wood products. Without any doubt, any adhesive that suffers creep rupture under typical service conditions clearly cannot be regarded as a structural adhesive. A ruptured bond line clearly means that structural failure has occurred.

A comparison of the European (CEN), ASTM and the proposed ISO/Canadian standard test methods are listed in the following table.

Brief description of test or specification	CEN	ASTM	Canada/ISO (Canada and ISO differ only to the extent that ASTM D4502 has been added to the draft ISO document)
Block shear test in compression loading	No corresponding test in CEN	D905 Shear strength in compression (block shear) intended as an evaluation of adhesives for wood. It is purely a test method and gives no pass/fail criteria. See D2559 for pass/fail criteria. No special climatic treatment.	ISO 12569/CSAO112.9. Shear strength in compression (block shear) intended as a test for adhesives. Test is conducted <ul style="list-style-type: none"> • dry, • wet after vacuum-pressure soak (vacuum 75 kPa for 30 minutes, 540 kPa for 2 hours) • wet after (boil 4 hours, dry 60°C for 19 hours, freeze - 30°C for 4 hours) repeated 7 times then boil for 4 hours, cooled and tested wet The strength and wood fibre failure pass/fail criteria differ for each condition.
Tension shear test with grain in central 3 ply specimen at 90° to face plies.	No corresponding test in CEN	D906 Shear strength in tension intended as evaluation of adhesive bonds in plywood. Purely a test method with no pass/fail criteria. No special climatic treatments.	
Tension shear test with grain in 2 ply specimen both parallel.	EN 302 but specimen size differs and the specimen is subjected to rather severe climatic treatment; see below.	D906 Shear strength in tension intended as evaluation of adhesive bonds in plywood. Purely a test method with no pass/fail criteria. No special climatic treatments.	
Specification for exterior use adhesives	<p>prEN WG4 01.7 sets out requirements for PURs in Service Classes 1 (interior), 2 (covered outdoor), 3 (full exposure). The designation indicates that the standard is still a working group document. All tests conducted on beech specimens with a density of 700kg/m³ – approximately that of Victorian Ash.</p> <p>Sets criteria for the following.</p> <ol style="list-style-type: none"> 1. Tensile shear strength (beech) in bond lines 0.1 mm and 0.5 mm thick. No wood failure criteria. Mean values range from 6 MPa to 10 MPa for 0.1 mm bond lines depending on various pre-treatments A1 20/65 for 7 days, A2 = A1 + 4 day soak – test wet, A3 = A2 A2 + 7 days dry – test dry, A4 = A1 + 6 hour boil + 2 hour soak – test wet, A5 = A4 + 7 day dry – test dry 2. Resistance to delamination – criteria for pass/fail only. Test method given in after treatments given in EN302. <u>Stage 1</u> vacuum 25 kPa for 5 minutes, pressure 600 kPa for 60m minutes, then repeat stage 1. <u>Stage 2</u> Dry for 22 hours at 65°C, RH < 15%. <u>Stage 3</u> Repeat Stages 1 and 2 twice more. The delamination percentage shall not exceed 5% on any single bond line. 3. Sets creep test criteria. The test is a modified version of D3535 – smaller specimen (6 glue lines; see Figure 5), 3 sets of conditions involving different specimens 	<p>D2559.</p> <ol style="list-style-type: none"> 1. Compression (block) shear of bond lines in various North American species at wood moisture contents of 8%, 12%, 16%. There are no wood failure criteria given in D2559 even though D906 requires wood failure values be recorded. Mean strength values at 12% mc range from 5.8 MPa for redwood to 12.4 MPa for white oak. 2. Resistance to delamination - criteria for pass/fail and test method. <u>Cycle 1</u> - vacuum 85kPa for 5 minutes, 520 kPa pressure 60 min, repeat cycle, dry for 21.5 hrs at 65°C. <u>Cycle 2</u> - heat the specimen with steam at 100°C for 90 min, place in tap water under pressure 520 kPa for 40 min. <u>Repeat Cycle 1</u>. The delamination percentage shall not exceed 1% of any softwood or 1.6% of any hardwood bond line. 3. Sets criteria for creep tests conducted in accordance with D3535 which requires separate test specimens with two conditioning treatments be conducted at 70°C 	<p>ISO 12569/CSAO112.9. Billets 19 x 140 x 400 in softwood hardwood respectively. Permitted percentages in any one bond line are 1.6% for hardwood and 1% for softwoods. Treatment is [(vacuum 75 kPa for 2 hours, pressure 540 kPa for 2 hours) x 2, dry for 88 hours at 28°C] x 2.</p> <p>ISO 12569/CSAO112.9. Sets creep deformation criteria under four separate environments – A, B₁, C (0.05 mm average with no single bond line exceeding 0.25 mm) and</p>

	<p>4. Sets criteria for tensile strength perpendicular to the grain strength must exceed 5 MPa. EN302 sets out the test procedure. Climatic treatments are for <u>Type I</u> adhesive – water impregnation 2¼ hours pressure to 600kPa, dry @ 28°C 96 hours – 2 cycles, <u>Type II</u> adhesive – water impregnation 2 hours 5 minutes, pressure to 600kPa, dry @ 65°C 22 hours – 3 cycles.</p> <p>5. Effect of wood shrinkage on shear strength. Specimens' wood is conditioned until moisture content is 16-18%. Specimens are dried 40°C, 30%RH until mc reaches 6-8% then stored at 20°C, 65%RH for 2 weeks and tested in compression shear.</p>	<p>and ambient RH – 7 days and 27°C, RH 90% - 7 days, shear stress 1.7 MPa. The total creep displacement shall not exceed 3.6 mm on 15 bond lines – 0.24 mm average per bond line.</p> <p>4. No corresponding requirement in ASTM D2559</p> <p>5. No corresponding requirement in ASTM D2559</p>	<p>B₂ (0.6 mm average with no single bond line exceeding 2.9 mm) A 7 days at 20°C, RH 95% B₁ 7 days at 70°C, ambient RH B₂ 2 hours at 180°C, ambient RH C cold vacuum-pressure soak, wrap specimen to prevent moisture loss, 50°C for 28 days. Loading is 1.7 MPa, specimen is ASTM D3535 clone.</p>
Creep deformation	prEN WG4 02-2:2003 sets out the methods. Standard is still under development.	D 3535 Requires separate test specimens with two conditioning treatments be conducted at 70°C and ambient RH – 7 days and 27°C, RH 90% - 7 days, shear stress 1.7 MPa.	
Creep rupture		D4680 Block shear specimens are tested to failure and creep strain is measured simultaneously.	
Hydrolytic stability	No corresponding requirement in CEN standards.	D 4502 Uses chemical kinetics and the Arrhenius Law to predict how strength loss is accelerated as temperature increases. It should have no effect on adhesives that are hydrolytically stable. The test method is provided in ASTM but it is not a requirement in D2559.	ISO 12569/CSAO112.9. Specifies D 4502 test chemical kinetics and the Arrhenius Law to predict how strength loss is accelerated as temperature increases. It should have no effect on adhesives that are hydrolytically stable. The test method is provided in ASTM but it is not a requirement in D2559.

Conclusions

There is a growing interest, both in Australia, and internationally, in the use of isocyanate-based adhesives for the production of structural wood components for application in a number of different service-life environments, including full exterior exposure. This interest has been driven by a number of potential advantages that these adhesives offer compared to the traditionally used phenolic and resorcinol resins. These include:

- a clear glue line
- lower resin usage
- 100% solids and hence no water to be removed from the glue line, opening up the possibility of gluing at higher wood moisture contents
- shorter cure times and hence potential increases in processing efficiencies
- no mixing of glue batches, minimising waste and reducing handling costs
- the possibility of gluing timbers that have been traditionally difficult to glue with PRF resins.

The potential benefits of these adhesives have sparked increased activity in both the fundamental research of adhesive bonding and the development of standards for application of these adhesives.

The large upsurge in interest in the adhesive scientific community has focused on the microscopic and molecular mechanisms of wood adhesion. This has extended to the topic of what makes a wood-adhesive bond durable. This research has grown over the last few years as evidenced by the number of papers presented at the Wood Adhesives 2005 symposium. One of the research topics currently being addressed is the lack of wood fibre failure when these adhesives are tested wet. The argument that isocyanate-based adhesives chemically bond with wood appears to have finally been put to rest with several groups independently determining that the isocyanate adhesive does not react with the chemical components of the wood in normal industrial operating conditions but rather with the water that is present in the wood to form an interpenetrating network within the wood to give a good mechanical interlock.

One component, 100% solids, moisture curing isocyanate adhesives have been recently approved for use in exterior structural applications in Europe following extensive testing. There are now several examples of building that have been constructed using wood-based structures bonded with these adhesives. The adhesives now have more than 13 years worth of service history in Europe. The European standard EN 301/302 has been extended to include these adhesives, provided that they meet the requirement of a series of additional tests focusing on their creep behaviour. These tests have been introduced after recent investigations highlighted that some of the adhesive formulations experience significant creep at higher temperatures. For approval for exterior structural use in the United States, adhesives must pass ASTM D2559 which is regarded as a severe test of durability. ASTM D3434, the Automatic Boil Test, is regarded as a good indicator of the durability of an adhesive and has shown a very good correlation with up to 13 years worth of results from several exposure test sites. This test method is also used in the USA as a screening test for determining the likely durable performance of new adhesives. The general trend for

the development of new standards has been to create performance criteria that any new adhesive must meet. This is in contrast to the traditional standards that have been more prescriptive. This is the approach that the ISO committee is using for its adhesive standard.

There are a number of potential occupational health and safety issues in using isocyanate-based adhesives. The principal risk in using these chemicals is that they are irritants and respiratory-tract sensitisers. The Australian Government's National Occupational and Safety Commission (NOSC) has defined the permissible levels of isocyanate exposure to be $0.02\text{mg}/\text{m}^3$ on a Time Weighted Average (TWA) with a Short Term Exposure Limit (STEL) of $0.07\text{mg}/\text{m}^3$. The principal component in these adhesives is likely to be MDI, which itself has a very low vapour pressure. The risk in using these materials arises when there is a chance of making them airborne by volatilizing the adhesive or creating an aerosol of the adhesive (or particulates contaminated with the adhesive) by, for example, spraying. Such conditions are likely to exist when this product is used in the manufacture of composite wood products such as MDF, particleboard or OSB. Such a risk is significantly reduced when it is used in the manufacture of engineered wood products where it is typically applied as a liquid. Recent studies have indicated that the level of isocyanate present when used in these applications is well below the levels recommended by NOSC. These risks can be further reduced by introducing the appropriate occupational health systems and practices when these adhesives are used.

In summary, the use of the isocyanate based adhesives for the production of structural wood products is growing internationally, even in the production of exterior-grade products where there is now a 13 year service history. This is occurring in tandem with the development of performance-based standards for wood adhesives. The next stage is to determine the performance characteristics of these adhesives in Australian conditions using Australian timber species. This is the next stage of the project "*Durability of isocyanate-based adhesives in engineered wood products*" funded by the Forest and Wood Products Research and Development Corporation (FWPRDC) and the Queensland Government Department of State Development and Innovation.

**APPENDIX A. Report on European and USA visit by
Milner July 2005**

Report on European and USA visit by Milner July 2005

A1 Itinerary

Day	Date	Activity
Saturday	2/7	Travel Melbourne to Zurich via Singapore and London
Sunday	3/7	
Monday	4/7	Visit FMPA, Zurich (am), Presentation by Prof Borimir Radović at Collano Headquarters, Sempach, Switzerland (pm)
Tuesday	5/7	Travel to Stuttgart, visit Dr Simon Aicher, FMPA
Wednesday	6/7	Train to Munich, car to Salzburg visit SHI near Salzburg, Austria
Thursday	7/7	Travel to Doka (near Vienna), continue to Vienna
Friday	8/7	Visit BOKU, Vienna (am), free (pm)
Saturday	9/7	Travel Vienna to Bar Harbor, Maine (USA). Bar Harbor is north of Boston
Sunday	10/7	Free
Monday	11/7	3 rd International Conference Advanced Wood Composites, Bar Harbor, Maine
Tuesday	12/7	
Wednesday	13/7	
Thursday	14/7	Visit University of Maine, Advanced Wood Composites Center
Friday	15/7	Free
Saturday	16/7	Return to Bangor to Melbourne via Boston, Los Angeles, Sydney
Sunday	17/7	

A2 Presentation by Prof Radović⁷⁷ (ex FMPA) (4/7/05)

History of polyurethanes in Europe

Single component PUR adhesives were developed in Europe as structural wood adhesives principally by Collano/Purbond. FMPA⁷⁸ was contacted in the early 1990s to determine if such adhesives could be used in structural in products such as glulam, finger jointed timber and I-joists⁷⁹. Due to the extensive use of polyurethanes (originally discovered by Otto Bayer in the 1930s) in the soles of shoes, as medical implants and other products they have always been regarded as hydrolytically stable.

Creep

During the period from 1990 through 2000 FMPA developed the test protocols for PURs that are now appearing in draft Euro (CEN) standards. Provided PURs meet the

⁷⁷ Prof Borimir Radović is a former Head of Department of Timber at the Otto Graf Institute, University of Stuttgart, Germany (also known as FMPA). Its expertise in wood gluing has resulted in its approval of new wood adhesives as being definitive largely due to Radović's efforts.

⁷⁸ The Materials Testing Institute University of Stuttgart (MPA Stuttgart, Otto-Graf-Institute (FMPA)) is located at the University of Stuttgart. It has been successful in materials testing and materials research in nearly all fields of mechanical engineering and civil engineering.

⁷⁹ PUR bonded I-joists are already being used structurally in the Australian market place in spite of having no recognition in Australian standards

requirements of what are now the current EN 301/302 standards and additional creep rupture and creep deformation/rupture tests now detailed in draft CEN standards, they will perform adequately as structural adhesives in Service Class 3 (SC3) exposure conditions. SC3 conditions means full outdoor exposure.

The creep tests are conducted at temperatures to the upper limit deemed possible under SC3 conditions (80°C) due to the fact that the creep behaviour of PURs is known to be temperature dependent. Two types of creep tests are commonly used

- creep deformation
- creep rupture

In the former, specimens are placed under constant load and the amount of relative movement in two bonded pieces is observed. In the latter, specimens are tested to failure during a short term test then specimens are loaded at 90%, 80% etc and the times to failure are observed.

With a creep deformation test, the amount of creep that can be tolerated is a function of the product in which the adhesive is to be used. Thus glulam is quite tolerant when it comes to creep deformation in the face joints but products such as oriented strand board (OSB) would not be. Creep rupture is, of course, unacceptable with any type of product. Bond line failure is synonymous with structural failure. Any testing of it would need to be conducted at load levels that are not unrealistically high.

Given the limits set for pass/fail criteria in the creep deformation tests devised by Radović, I questioned whether or not there was a rational reason why this test is always necessary. According to Radović and his successor at FMPA, Aicher, it seems that that creep deformation tests are included only because they were traditionally used to test plastic adhesives. However, the creep limits set (0.05 mm) are so low that they have no significant effect on structural performance with products such as glulam. On the other hand, in products such as OSB with thin wafers separated by multiple bond lines the cumulative effect of creep would destroy the structural properties. Both Radović and Aicher defended the use of the creep deformation as a screen for PURs but could not advance a reason, based on structural engineering arguments, for its retention. It would seem wise to retain the test, however, given the body of world opinion that it is a good idea even if nobody quite knows why.

Hydrolytic stability

Initially, I wrote this section of my report under a heading, “durability”, with the intention of describing any hydrolysing chemical reaction that might lead to a loss of bond strength. This creates the impression that problems associated with adhesive bond durability are purely chemical in nature when, in fact, there are many factors at play. Nevertheless hydrolytic stability is an absolutely essential requirement for a viable structural wood adhesive.

The extension of the CEN standards is limited to the coverage of single component PURs only and does not cover other adhesive types. Because PURs have always been regarded as hydrolytically stable by Europeans there has never been any perceived need for any form of hydrolytic stability test.

Other advantages of PURs

Radović was very positive about the advantages of one-component PURs that met EN301/302 and the additional creep criteria. These included

- reduction in waste and environmental friendliness,
- new developments in finger jointing and associated technology that eliminated potential production problems such as glueless finger joints.

The latter is a very convincing argument in favour of PURs. The viscosity has been adjusted such that beads can be applied to the finger tips with the bead application spread confirmed by computer monitoring and the spread on to the fingers occurring during pressing. This overcomes a major concern with existing finger jointing technology as currently implemented in Australia. Current European technology makes our local industry look technologically backward and the existing Australian standards are largely to blame. Extracts from his power point presentation follow.

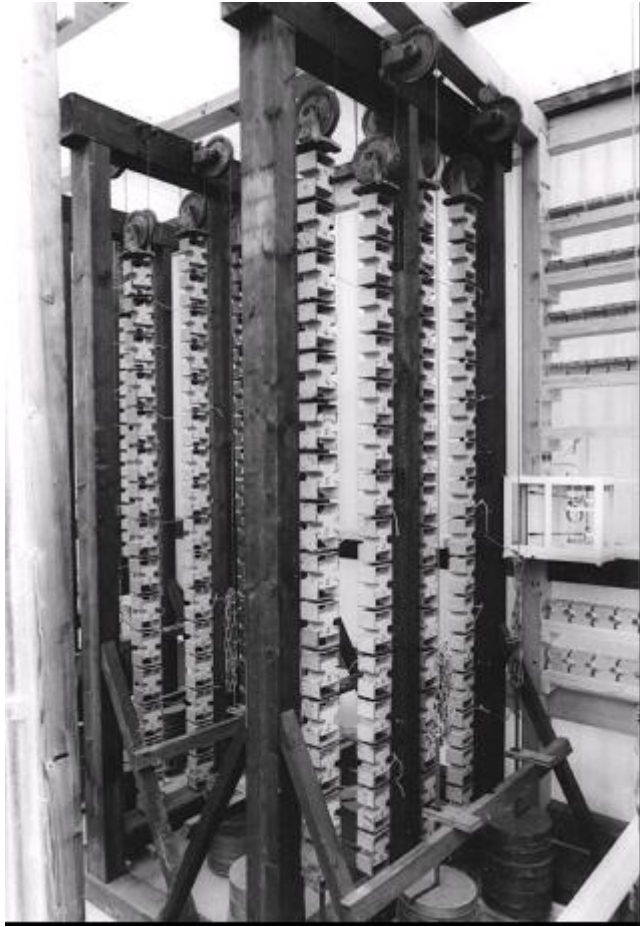
Application system for Finger-Joint production

- **No contact with the wood**
- **One-side application**
- **Opto-electronic monitoring**

(KEBA-system)



Method of applying adhesive



Rigs to monitor long term tension capacity – a form of creep rupture.

Another interesting feature was the newer test rigs used to monitor creep deformation in beams. The specimens were 500 x 50 x 50 mm with a single bond line which meant that much less dead load was required.

A4 SHI (6/7/05)

SHI is a glulam manufacturer near Salzburg, whose entire production (finger, side and face bonds) involve the use of PURs. It produces 35,000 m³ per annum which is twice the entire Australian production. The glulam is used locally in Austria but also exported to Germany, Italy, Austria and elsewhere including countries outside Europe. It has no control of where its product goes which means that it will certainly find application in Service Class 3 conditions (full outdoor exposure).

A DVD video clip is available showing the production system.

A5 Doka (7/7/05)

Doka headquarters are near Vienna, Austria. Doka produce PUR bonded products for the concrete formwork industries as well as shop-fitting components. More details of the Doka operation are given in the body of the literature review.

A6 Micromechanics of bond failure (Meuller and Gindl, BOKU, Vienna) (8/7/05)

Meuller and Gindl are investigating the micromechanics of PURs and it seemed that they are on the right track when it comes to identifying how wood adhesives should be modified to obtain better performance.

Meuller and Gindl are both committed to the investigation of PRFs and PUs and seeking to identify reasons why PUs, when dry, are usually stronger than PRFs and exhibit the same level of wood failure but, when tested wet, drop in strength to levels almost the same as PRFs tested wet but have much lower levels of wood failure. A major focus of their research is to investigate why this is so. (PU performance with respect to wood failure is enhanced by coating the surface of wood with a so-called HMR primer and this has become standard practice when bonding plastic composites to wood.)

Gindl highlighted the fact that adhesives need to penetrate the first two cell layers to achieve mechanical interlock. Gindl and Meuller between them have used nano-indentation techniques to obtain elastic moduli of wood constituents, speckled laser interferometry (Michelson interferometry) to investigate the strain distributions in the bond layer, interphase region and the wood zones below. The surface strain measurement equipment used is produced by Dantec Ettemeyer in Germany and is especially sensitive, allowing them to obtain very accurate measurements. Other techniques are used to investigate adhesive diffusion into cell walls as reported above.

A7 Gardner (12/7/05)

At the Third International Conference on Advanced engineered Wood Composites, Gardner presented a paper outlining the fundamental wood bonding mechanisms.

Mechanical inter-locking, whereby the adhesive flows into wood cavities in the cellular structure and forms microscopic keys. This mechanism is thought to be the dominant contributor to wood bond strength. The cells at the interface are inevitably damaged even by the most careful of methods and this damage may extend even more deeply with poor machining. It is important that the adhesive penetrates at least 2 cell layers below the interface to form the necessary interlocks.

Diffusion, whereby long chain molecules in the wood and cell walls intertwine without necessarily forming any sort of chemical bond. Gindl (see below) pointed out that evidence exists that PRFs do this more effectively than PURs although this may be a mixed blessing. PRFs have a relatively high modulus of elasticity and by diffusing into the cell walls create stress concentrations and a large number of fracture sites leading to high wood failure levels. PURs do not diffuse significantly into cell walls and have a low modulus of elasticity (around 1/100 that of cell walls) and thus less of a tendency to generate fracture sites. The notion that wood failure is not necessarily a good thing is gaining credence among some European researchers.

Electrostatic or Van der Waal forces, which are well known to school children who pick up pieces of paper after rubbing a plastic ruler against articles of clothing. These

forces are not regarded as significant with wood to wood or wood to composites bonding.

Covalent bonding which is a true chemical reaction between the surfaces being bonded – electrons shared between atoms. No conclusive evidence has been found to support the view that PURs covalently bond with any wood chemical components (cellulose, lignin etc).

Weak forces are formed with oils, preservatives which arise from processing operations or contamination and extractives naturally present in the wood substrates. Such bonds are detrimental and, worse still, may inhibit the flow of adhesives into the wood cells.

A8 Private discussions and conclusions drawn from Gardner and the BOKU researchers

The following conclusions came out of discussions with Gardner and the BOKU people.

1. PUs are, in all probability, hydrolytically stable. It is unlikely that any hydrolytic weaknesses will be found, ie, chemical degradation is unlikely to be an issue. In further support of this view, it is noted that CEN standards that have been extended to cover PUs do not contain any form of hydrolytic stability test.
2. Problems could exist with the creep of some PUs at higher temperatures. Radovic reported that, in window frames, in Europe, temperatures as high as 80°C have been recorded in strong sunlight and that creep deformation may be sharply higher at such temperatures. It will be essential in our outdoor exposure trials that weather conditions, deflections and possibly bond line temperatures be taken. In larger structural members, it is unlikely that high temperatures will be observed at glue lines given the good insulating properties of wood.
3. The hydromechanical response of PUs has not been investigated by Gardner and his colleagues at University of Maine. Gardner reported at the AEWG conference that he regarded this as an important investigation. The thin films produced at Monash just prior to leaving for Europe were shown to Gardner (UMaine) and Frazier (West Virginia Tech) who both said they were of good quality and would be useful in any investigation. This work should clearly proceed as proposed.
4. The BOKU work at their (Institute for Wood Research, Vienna) appeared to be well focussed on the critical issue of wood bonding micromechanics. Gardner told me that he was spending a sabbatical there with them. For the current project to focus also on this, which I consider to be a good idea, equipment for nano-indentation (to measure elastic moduli of the wood components) and to measure adhesive diffusion levels will be essential. Some equipment may already be available at Monash or CSIRO.

5. The Dantec-Emmeteyer speckled laser interferometry equipment certainly has done a good job for the BOKU researchers but is not without problems. It requires high level skills to operate correctly, is very sensitive to vibrations in adjacent regions and can only repeat measurements at a rate of 0.4Hz. This low repeat rate is a disadvantage when it come to following a fracture sequence which may be proceeding rapidly. Meuller also claimed that it took 6 months for the BOKU people to get good results from the equipment. Digital image correlation equipment produced by GOM is used by UMaine researchers and is based on photogrammetry. The reported accuracy is not as good as the Dantec equipment (an order of magnitude worse according to the BOKU people) but it can undertake repeat scans at much higher rates (around 8Hz) making it possible to track crack propagation. UMaine have 1.3 megapixel cameras and we would propose buying a system with 4 megapixel cameras which should improve the accuracy. A problem with making this decision at present is that Dantec report being able to read strains only to 200 μ which is the same claim made by GOM but it is in conflict with what the BOKU researchers tell me. More enquiries are necessary and these need to be made directly with Dantec and GOM directly rather than through intermediaries. The UMaine people tell me that GOM also offers a discount to Universities, a matter yet to be pursued with not only them but also Dantec.

6. The size of the outdoor exposure specimens can be reduced. The Otto Graff Institute at Stuttgart University in Germany undertakes tests on members of cross-section 50 x 50 and length 700 *mm* with a single glue line as opposed to the 6 laminate beams 150 x 35 and length 1500 *mm* proposed initially. The size of the rigs can be made much smaller.